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(21)Application number : 05-267971 (71)Applicant : TDK CORP

(22)Date of filing : 30.09.1993 (72)Inventor : SUZUKI KAZUAKI
FURUBAYASHI MAKOTO
MIURA TARO
KAWAMURA KEIZO

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(54) MULTI-LAYER CERAMIC COMPONENT

(57)Abstract:

PURPOSE: To improve the characteristic such as Q value by forming an internal pattern onto a specific dielectric ceramic material layer, laminating the layer onto a dielectric ceramic material layer and baking the laminated component at a temperature over the melting point of an inner conductor and below the boiling point.

CONSTITUTION: The multi-layer ceramic component is manufactured by forming an inner conductor pattern onto a green sheet made of a dielectric ceramic material, laminating green sheets, pressing through hot press and baking the pressed sheets. In this case, the dielectric ceramic material whose sintering end temperature obtained by a thermal contraction curve at a temperature rising rate of 200°C/hour is temperature over the melting point of the inner conductor. The sintering end temperature is a cross point F between tangential lines III, IV in the thermal contraction curve of the ceramic material. Thus, the structure of the inner conductor is made tight, the contact state of the conductor is improved and the Q value is enhanced.

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CLAIMS

[Claim(s)]

[Claim 1] They are the multilayer ceramic components which have an inner conductor layer and two or more dielectric ceramic layers. The dielectric ceramic ingredient layer of the dielectric ceramic ingredient of the oxide whose sintering termination temperature searched for from the heat shrink curve in the programming rate of 200 degrees C/hour is the temperature below the boiling point more than the melting point of an inner conductor is prepared. The multilayer ceramic components which formed the pattern of an inner conductor on this dielectric ceramic ingredient layer, carried out the laminating of this to said dielectric ceramic ingredient layer further, and were calcinated and obtained at the temperature more than the melting point of said inner conductor.

[Claim 2] The multilayer ceramic components of claim 1 said whose burning

temperature is the temperature beyond said sintering termination temperature.

[Claim 3] The multilayer ceramic components of claims 1 or 2 whose specific inductive capacity epsilon in the temperature of 20 degrees C of said dielectric ceramic ingredient is 6.5-120.

[Claim 4] Said dielectric ceramic ingredient is MgO-SiO₂. A system and CaO-MgO-TiO₂ System, BaO-TiO₂-SnO₂ A system and BaO-MgO-CoO-Nb₂O₅ System, A BaO-Nd₂O₃-TiO₂-Bi₂O₃-aluminum₂O₃-MnO system, BaO-MgO-Ta₂O₅ A system and ZrO₂-SnO₂-TiO₂ System, PbO-CaO-ZrO₂ A system and SrO-ZrO₂-TiO₂ System, BaO-Sm₂O₅-TiO₂ A system and PbO-BaO-Nd₂O₃-TiO₂ A system and Li₂O-Na₂O-Sm₂O₅-TiO₂ One multilayer ceramic components of claims 1-3 which are either of the systems.

[Claim 5] The metals which constitute said inner conductor are one multilayer ceramic components of claims 1-4 whose contents of silver or copper are a thing beyond 90wt%.

[Claim 6] The metal which constitutes said inner conductor is silver, and it is 1×10^{-1} atm. One multilayer ceramic components of claims 1-5 calcinated and obtained under the following oxygen tension.

[Claim 7] It has a dielectric ceramic layer in the outermost layer, and the distance from said outermost layer side front face of said inner conductor layer to said outermost layer front face is 500 micrometers. Multilayer ceramic components of claim 6 which is the following.

[Claim 8] Said dielectric ceramic ingredient is CaO-MgO-TiO₂. A system and BaO-TiO₂-SnO₂ System, A BaO-Nd₂O₃-TiO₂-Bi₂O₃-aluminum₂O₃-MnO system, BaO-MgO-Ta₂O₅ A system and ZrO₂-SnO₂-TiO₂ System, SrO-ZrO₂-TiO₂ A system, BaO-Sm₂O₅-TiO₂ system, PbO-BaO-Nd₂O₃-TiO₂ A system and Li₂O-Na₂O-Sm₂O₅-TiO₂ System, It is in ***** and is 1×10^{-4} atm. It exceeds and is 1×10^{-1} atm. Multilayer ceramic components of claims 6 or 7 calcinated and obtained under the following oxygen tension.

[Claim 9] The metal which constitutes said inner conductor is copper, and it is 1×10^{-6} atm. One multilayer ceramic components of claims 1-5 calcinated and

obtained under the following oxygen tension.

[Claim 10] A dielectric ceramic ingredient is MgO-SiO₂. A system and BaO-MgO-CoO-Nb₂O₅ A system and PbO-CaO-ZrO₂ Multilayer ceramic components of claim 9 which is either of the systems.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to multilayer ceramic components mainly used in a microwave range, such as a dielectric resonator and a filter.

[0002]

[Description of the Prior Art] A miniaturization of the dielectric resonator used especially in a microwave range is desired as the use frequency domain of multilayer ceramic components, for example, a dielectric resonator, is expanded. The dielectric ceramic ingredient for microwave is variously developed from such a request, and it is required that a high dielectric constant should be shown as what realizes especially a miniaturization.

[0003] Moreover, in order to make the resonance characteristic still higher, the

approach of carrying out the laminating of the ceramic ingredient is adopted, using conductor material suitable for microwave, such as Ag and Cu, as an internal electrode. When producing multilayer ceramic components, such as a resonator, the green sheet method and laminating print processes are used, and the approach of carrying out coincidence baking of conductor material and the ceramic ingredient is adopted.

[0004] In order to acquire sufficient property by such approach conventionally, it is thought that it is necessary to prevent melting of an inner conductor ingredient, and it was supposed. [it] [necessary] [to calcinate at the temperature below the melting point of an inner conductor ingredient] For this reason, it was presupposed that the ceramic ingredient with the need of calcinating at an elevated temperature could not be used even if high dielectric characteristics are shown. Consequently, various proposals are made about the dielectric ceramic ingredient in which low-temperature baking is possible (JP,3-295854,A, JP,3-295855,A, JP,3-295856,A, JP,3-295858,A, JP,3-295859,A, etc.).

[0005] When examination is variously added to the above-mentioned conventional method, however, this invention persons By carrying out coincidence baking at the temperature more than the melting point of an inner conductor ingredient, an inner conductor fuses and carries out eburnation. The grain boundary in the inner conductor produced with conducting powder can be extinguished substantially. It has found out that improvement in a property, such as improving the Q value as a resonator, can be aimed at, and various proposals are performed (Japanese Patent Application No. No. 306760 [three to], 4-134199, 4-146478, 3-360323, 4-313997).

[0006] However, the ceramic ingredient for low-temperature baking is used for these, when fusing and calcinating the above-mentioned inner conductor using such a ceramic ingredient, probably because the front-face nature of an inner conductor is not good, it especially originates in various factors, there is a problem that the Q value as a resonator tends to fall, and an improvement of this point is desired.

[0007] In addition, in JP,2-197189,A, calcinating the alumimium nitride circuit board which formed the inner conductor using one or more sorts in gold, silver, and copper is proposed. The burning temperature with the optimal alumimium nitride circuit board is more than the melting temperature of the above-mentioned inner conductor, and fuses these inner conductors substantially at the time of baking. even if it uses gold, silver, and an inner conductor ingredient with comparatively low melting temperature like copper by this proposal using the earliness of the wettability badness and the eburnation rate which alumimium nitride has etc. -- the alumimium nitride circuit board -- as an internal wiring material -- a conductor -- it is supposed that the circuit was able to be formed. And it is thought in this case that the eburnation of the inner conductor by the same melting has arisen also in this invention.

[0008] However, there is no example which manufactured the multilayer ceramic components for RFs (for example, 200MHz - 10GHz frequency of extent), such as a resonator, using such alumimium nitride, for example. In the components for RFs with which a miniaturization is desired, generally, it is hard to use an ingredient with a comparatively low dielectric constant like alumimium nitride, and even if it uses it, it will be enlarged. Furthermore, the wettability of alumimium nitride to molten metal is bad. For this reason, although the eburnation of an inner conductor is produced, in that interface, it is easy to produce a defect, and when excessive, the constriction of a conductor pattern and an open circuit arise. With the components for [which is asked for the miniaturization] RFs, with the lamination of a dielectric layer, when lamination and narrow thinning are called for and it is going to carry out especially lamination and narrow thinning, generating of defects, such as an open circuit of an inner conductor layer, also actualizes the thickness and width of face of an inner conductor layer.

[0009] Moreover, on the occasion of baking of laminating composite part with the still thinner thickness of the dielectric ceramic ingredient layer between an inner conductor and a bill-of-materials stratification plane etc., many defectives with which an inner conductor and a dielectric ceramic ingredient layer exfoliate are

generated, using an oxide as a dielectric ceramic ingredient, using silver especially as an inner conductor.

[0010]

[Problem(s) to be Solved by the Invention] As a result of being able to carry out eburnation of the inner conductor and being able to make front-face nature good moreover, using the dielectric ceramic ingredient excellent in a dielectric constant and dielectric loss (Q-f), the purpose of this invention can aim at improvement in properties, such as Q value, and is to offer multilayer ceramic components with little generating of the defective by exfoliation with an inner conductor layer and a dielectric ceramic ingredient layer, an open circuit of an inner conductor layer, etc. further at the time of baking.

[0011]

[Means for Solving the Problem] Such a purpose is attained by this invention of following the (1) - (10).

(1) They are the multilayer ceramic components which have an inner conductor layer and two or more dielectric ceramic layers. The dielectric ceramic ingredient layer of the dielectric ceramic ingredient of the oxide whose sintering termination temperature searched for from the heat shrink curve in the programming rate of 200 degrees C/hour is the temperature below the boiling point more than the melting point of an inner conductor is prepared. The multilayer ceramic components which formed the pattern of an inner conductor on this dielectric ceramic ingredient layer, carried out the laminating of this to said dielectric ceramic ingredient layer further, and were calcinated and obtained at the temperature more than the melting point of said inner conductor.

(2) The multilayer ceramic components of the above (1) said whose burning temperature is the temperature beyond said sintering termination temperature.

(3) The above (1) or (2) multilayer ceramic components whose specific inductive capacity epsilon in the temperature of 20 degrees C of said dielectric ceramic ingredient is 6.5-120.

(4) Said dielectric ceramic ingredient is MgO-SiO₂. A system and CaO-MgO-

TiO₂ System, BaO-TiO₂-SnO₂ A system and BaO-MgO-CoO-Nb₂O₅ System, A BaO-Nd₂O₃-TiO₂-Bi₂O₃-aluminum₂O₃-MnO system, BaO-MgO-Ta₂O₅ A system and ZrO₂-SnO₂-TiO₂ System, PbO-CaO-ZrO₂ A system and SrO-ZrO₂-TiO₂ System, BaO-Sm₂O₅-TiO₂ A system and PbO-BaO-Nd₂O₃-TiO₂ A system and Li₂O-Na₂O-Sm₂O₅-TiO₂ One multilayer ceramic components of above-mentioned (1) - (3) which is either of the systems.

(5) The metals which constitute said inner conductor are one multilayer ceramic components of above-mentioned (1) - (4) whose contents of silver or copper are a thing beyond 90wt%.

(6) The metal which constitutes said inner conductor is silver, and it is 1x10⁻¹atm. One multilayer ceramic components of above-mentioned (1) - (5) calcinated and obtained under the following oxygen tension.

(7) It has a dielectric ceramic layer in the outermost layer, and the distance from said outermost layer side front face of said inner conductor layer to said outermost layer front face is 500 micrometers. Multilayer ceramic components of the above (6) which is the following.

(8) Said dielectric ceramic ingredient is CaO-MgO-TiO₂. System, BaO-TiO₂-SnO₂ A system, a BaO-Nd₂O₃-TiO₂-Bi₂O₃-aluminum₂O₃-MnO system, BaO-MgO-Ta₂O₅ A system and ZrO₂-SnO₂-TiO₂ System, SrO-ZrO₂-TiO₂ A system and BaO-Sm₂O₅-TiO₂ System, PbO-BaO-Nd₂O₃-TiO₂ A system and Li₂O-Na₂O-Sm₂O₅-TiO₂ System, It is in ***** and is 1x10⁻⁴atm. It exceeds and is 1x10⁻¹atm. The above (6) or (7) multilayer ceramic components which were calcinated and obtained under the following oxygen tension.

(9) The metal which constitutes said inner conductor is copper, and it is 1x10⁻⁶atm. One multilayer ceramic components of above-mentioned (1) - (5) calcinated and obtained under the following oxygen tension.

(10) A dielectric ceramic ingredient is MgO-SiO₂. A system and BaO-MgO-CoO-Nb₂O₅ A system and PbO-CaO-ZrO₂ Multilayer ceramic components of the above (9) which is either of the systems.

[0012]

[Elements of the Invention] Hereafter, the concrete configuration of this invention is explained to a detail.

[0013] After the multilayer ceramic components of this invention form an inner conductor pattern on the green sheet of a dielectric ceramic ingredient, they carry out the laminating of this green sheet, stick it by pressure with a heat press, are calcinated after that and manufactured. The so-called printing lamination which carries out the laminating of the paste of a dielectric besides such so-called green sheet method and the paste of an inner conductor by turns may be used.

[0014] In this case, in this invention, it is calcinating at the temperature more than the melting point of an inner conductor using the dielectric ceramic ingredient whose sintering termination temperature searched for from the heat shrink curve in the programming rate of 200 degrees C/hour is the temperature below the boiling point more than the melting point of an inner conductor. That is, the dielectric ceramic ingredient used for this invention is for the so-called elevated-temperature baking, and while an inner conductor fuses with baking, the description of this invention is in the place in which a ceramic ingredient forms a sintered compact. Therefore, in this invention, it is the temperature more than the melting point of an inner conductor, and calcinates at the temperature beyond the sintering termination temperature of a ceramic ingredient.

[0015] The "sintering termination temperature" said to this invention points out theoretically the temperature in which a ceramic ingredient forms a sintered compact, and it asks from a heat shrink curve like the after-mentioned (refer to after-mentioned drawing 1).

[0016] The sintering termination temperature in this invention is the temperature more than the melting point of an inner conductor, and is temperature with a melting point [of an inner conductor] of +150 degrees C or more especially preferably still more preferably preferably as mentioned above the melting point of +100 degrees C or more of an inner conductor the melting point of +50 degrees C or more of an inner conductor. Moreover, temperature T20' (drawing 1 : point G) which corresponds from Point C at 80% of place between the

sintering initiation temperature (drawing 1 : point C) searched for from the below-mentioned heat shrink curve and the sintering termination temperature T20 (drawing 1 : point F) has the desirable temperature more than the melting point of an inner conductor, temperature with a melting point [of an inner conductor] of +20 degrees C or more is still more desirable, and it is desirable that it is especially temperature with a melting point [of an inner conductor] of +50 degrees C or more. Moreover, since an inner conductor evaporates when it comes to an elevated temperature to the extent that vapor pressure becomes high too much, the upper limit of sintering termination temperature is made below into the boiling point of an inner conductor as mentioned above. Usually, 960-1900 degrees C of sintering termination temperature are about 1100-1700 degrees C preferably. In addition, the melting point of the inner conductor in the above and the boiling point are the melting point of an inner conductor metal (an alloy is also included.), and the boiling point, and are usually called for in the state of bulk.

[0017] Moreover, actual sintering temperature is made into the temperature beyond sintering termination temperature. However, this relation is materialized between the sintering termination temperature searched for from the heat shrink curve made into a programming rate and these conditions until it reaches an actual burning temperature. Moreover, the above-mentioned programming rate of 200 degrees C/hour is applied at the time of the usual baking. It sets, when it considers as the same programming rate, and it is the actual burning temperature T2. It is the same as the sintering termination temperature T20, or becomes the temperature of the range to temperature higher about 70 degrees C than this. Therefore, the melting point mp of T2, T20, and an inner conductor is $mp \leq T20 \leq T2$. It is desirable to have a relation.

[0018] Thus, since the multilayer ceramic components of this invention are calcinated at the temperature beyond the sintering termination temperature of a dielectric ceramic ingredient using what is sintered at the temperature more than the melting point of an inner conductor as a dielectric ceramic ingredient, they

can discharge the gas which occurs from an inner conductor at the time of baking out of a dielectric ceramic ingredient layer. Therefore, there is no irregularity in a front face and a surface state can form a good inner conductor in it. For this reason, properties, such as Q value as a resonator, become high. In addition, the gas which occurs at this time is gas which occurs at the time of baking, originates in vehicles, such as a binder and a solvent, for example, occurs, such as carbon dioxide gas and moisture.

[0019] Moreover, when carrying out the laminating of the inner conductor to a dielectric ceramic ingredient layer and adopting the approach of carrying out coincidence baking conventionally, in order to prevent melting of an inner conductor, it is supposed that the ceramic ingredient sintered at temperature higher than the melting point of an inner conductor cannot be used, and it was presupposed that it could not use since burning temperature is high even if it is the ingredient excellent in a dielectric constant, and Q and f value (JP,3-290358,A etc.). However, in this invention, by making an inner conductor into a melting condition, eburnation of the structure of an inner conductor was carried out, the contact condition of a conductor has been improved, loss of a track was reduced, and the effectiveness of raising the Q value as a resonator has been acquired. For this reason, sintering temperature can be high, and can use the ceramic ingredient excellent in a dielectric constant, and Q and f value, can employ the high property of the ceramic ingredient itself efficiently, and can make Q value as a resonator high.

[0020] In addition, if it becomes the temperature which the effectiveness that the front-face nature of an inner conductor will improve if said sintering termination temperature turns into temperature of under the melting point of an inner conductor is no longer acquired, and, on the other hand, surpasses the boiling point of an inner conductor, an inner conductor will disappear. Moreover, if burning temperature turns into temperature of under the melting point of an inner conductor, sintering a ceramic ingredient has not been continued and the effectiveness by inner conductor melting will not be acquired.

[0021] The aforementioned "sintering termination temperature" is searched for from a heat shrink curve as shown in drawing 1 . As shown in drawing 1 , a ceramic ingredient has a certain inclination with the rise of temperature, and although thermal expansion is carried out, if it becomes a certain temperature, it will begin to shift from the inclination. The point in a heat shrink curve is set to A. It passes over an A point, and it begins to contract and it is begun to contract a ceramic ingredient at a fixed rate. The point by the side of the maximum low temperature of the field contracted at a fixed rate is set to B. Moreover, the point by the side of the maximum elevated temperature of the field contracted at a fixed rate is set to D. Furthermore, contraction is completed and the point by the side of the maximum low temperature is set to E among the fields considered that there is almost no volume change.

[0022] And tangent [in / for the intersection C of the tangent I in Point A, and the tangent II in Point B / sintering initiation temperature and Point D] III The intersection F with the tangent IV in Point E is defined as the sintering termination temperature T20.

[0023] If the conditions which sintering termination temperature described above are fulfilled as a dielectric ceramic ingredient used for the multilayer ceramic components of this invention, originally you may be what kind of thing, and it will not limit especially. However, 200MHz - 10GHz When using as dielectric layers, such as a resonator for RFs treating the frequency of extent, there is no example which used the nitride, the ceramic of a silicon carbide system, etc. for the dielectric ceramic ingredient calcinated and obtained. Moreover, with the ceramic of a nitride or a silicon carbide system, wettability with molten metal, such as an alloy containing those ingredients, the silver used as an inner conductor and copper, or them, is bad. With the multilayer ceramic components in a miniaturization and the inclination which carries out lamination, the inner conductor layer is also thin in thickness, and the need of also narrowing width of face is high further. On the occasion of baking of such multilayer ceramic components, the incidence rate of defects, such as an open circuit of an inner

conductor layer, tends to become high in the dielectric ceramic layer using a wettability bad ceramic ingredient. Therefore, as a dielectric ceramic ingredient, wettability is more high and the thing which has the low incidence rate of defects, such as an open circuit of an inner conductor layer, and which serves as mixture of an oxide or an oxide by baking is desirable. For example, they are the multiple oxide calcinated and obtained using the ingredient system mentioned later, the mixture of the oxide which has rutile structure etc. in a part, etc. This inventions are multilayer ceramic components with the dielectric ceramic layer of the mixture of an oxide or an oxide which calcinated such a dielectric ceramic ingredient and was obtained.

[0024] As an example of the dielectric ceramic ingredient used for this invention, it is MgO-SiO₂. A system and CaO-MgO-TiO₂ A system and BaO-TiO₂-SnO₂ A system and BaO-MgO-CoO-Nb₂O₅ A system, a BaO-Nd₂O₃-TiO₂-Bi₂O₃-aluminum₂O₃-MnO system, etc. are mentioned. MgO-SiO₂ As a system, it is 2 MgO-SiO₂ 30-95-mol %, less than [CaTiO₃ 50 mol %], and less than [SrTiO₃ 60 mol %]. As opposed to a total of 100-mol% of each [these] oxide MgO 0.1 - 10wt%, La₂O₃ 0.1 - 10wt% -- added thing (refer to JP,47-21698,A);CaO-MgO-TiO₂ As a system At MgTiO₃ 70-100-mol % and TiO₂ 0-30-mol % a total of 100-mol% of each [these] oxide -- receiving -- CaTiO₃ 1 - 9wt% -- added thing (JP,52-118599,A);BaO-TiO₂-SnO₂ As a system TiO₂ and BaO-x{(1-y) ySnO₂} [x=4-4.5, and thing (refer to JP,4-32483,B);BaO-MgO-CoO-Nb₂O₃ that has the presentation of y= 0 - 0.10] As a system BaO56.0 - 63.0wt%, CoO0.1 - 11.7wt%, As a Nb₂O₅ 31.0 - 34.7wt% thing (refer to JP,61-72676,A);BaO-Nd₂O₃-TiO₂-Bi₂O₃-aluminum₂O₃-MnO system, MgO0.1 - 6.5wt% 9-18 mol % and TiO₂ 65-73-mol % of BaO(s), At Nd₂O₃ 14-19-mol %, a total of 100-mol% of each [these] oxide is received. Bi₂O₃ 3.0 - 11.0wt% and aluminum₂O₃ 0.1 - 2.0wt% and MnO -- 0.1 - 1.0wt% -- it is what was added (Japanese Patent Application No. No. 327352 [three to] by these people). In addition, BaO-MgO-Ta₂O₅ A system and ZrO₂-SnO₂-TiO₂ A system and PbO-CaO-ZrO₂ A system and SrO-ZrO₂-TiO₂ A system, BaO-Sm₂O₅-TiO₂ system, and PbO-BaO-Nd₂O₃-TiO₂ A

system and $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{Sm}_2\text{O}_5-\text{TiO}_2$ A system etc. can be used.

[0025] $\text{BaO}-\text{MgO}-\text{Ta}_2\text{O}_5$ As a system, it is shown by the empirical formula of $\text{BaO}(\text{Mg}_{1-x}\text{Ta}_x)_3$ however $0.28 \leq x \leq 0.39$, and $0.98 \leq y \leq 1.00$, for example. $\text{ZrO}_2-\text{SnO}_2-\text{TiO}_2$ As a system, it is shown by TiO_4 , however the empirical formula of $0.1 \leq x \leq 0.3$, for example $(\text{Zr}_{1-x}\text{Sn}_x)$. $\text{PbO}-\text{CaO}-\text{ZrO}_2$ As a system, it is shown by ZrO_3 , however the empirical formula of $0.35 \leq x \leq 0.5$, for example $(\text{Pb}_{1-x}\text{Ca}_x)$. $\text{SrO}-\text{ZrO}_2-\text{TiO}_2$ As a system, it is shown by the empirical formula of $\text{SryO}(\text{Zr}_{1-x}\text{Ti}_x)_3$ however $0 \leq x \leq 0.1$, and $0.98 \leq y \leq 1.01$, for example. $\text{BaO}-\text{Sm}_2\text{O}_5-\text{TiO}_2$ as a system -- $x\text{BaO}-y\text{Sm}_2\text{O}_5-z\text{TiO}_2$ ***** -- it is the thing of $0.1 \leq x \leq 0.2$, $0.1 \leq y \leq 0.2$, and $0.6 \leq z \leq 0.75$. $\text{PbO}-\text{BaO}-\text{Nd}_2\text{O}_3-\text{TiO}_2$ as a system -- $x\text{BaO}-y\text{Nd}_2\text{O}_3-z\text{TiO}_2$ ***** -- $0.02 \leq x \leq 0.25$, $0.05 \leq y \leq 0.41$, and $0.50 \leq z \leq 0.82$ -- it is -- the sum total of each [these] component -- receiving -- further -- PbO -- less than [17wt%] -- it contains. $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{Sm}_2\text{O}_5-\text{TiO}_2$ As a system, it is shown by the empirical formula of $0.25 \leq x \leq 0.35$, $0.15 \leq y \leq 0.25$, and $0.4 \leq z \leq 0.6$, for example $(\text{Li}_x\text{Na}_y\text{Sm}_z)$ as TiO_3 , however $x+y+z=1$.

[0026] Moreover, in addition to the above-mentioned basic presentation, further, the need is accepted and it is MnO , CuO , ZnO , SnO_2 , PbO , NiO and WO_3 , SiO_2 , and B_2O_5 . And the Nb_2O_5 grade may be added.

[0027] Moreover, specific inductive capacity [in / in the above-mentioned dielectric ceramic ingredient / 20 degrees C] (epsilon) has 6.5-120, and the microwave dielectric characteristics 3500-225000, and whose resonance frequency temperature coefficient (tauf) especially 20-120, and dielectric loss (Q and f value) are -4.5-+8.5 ppm/degree C. In addition, it asks for tauf as a slope of a line which connected -40 degree C resonance frequency and the resonance frequency of 80 degrees C.

[0028] In this invention, although the ceramic ingredient which uses the aforementioned oxide aggregate as a principal component is used for the insulating dielectric ceramic ingredient layer which forms the pattern of an inner conductor paste, glass may be added suitably. Although addition glass changes with configurations of the oxide aggregate for example, in the thing of a $\text{BaO}-\text{Nd}_2$

O₃-TiO₂-Bi₂O₃-aluminum₂O₃-MnO system PbO -- 20 - 86.5wt% -- desirable -- 30 - 84wt% and B₂O₃ 8.5 - 21wt% -- desirable -- 9 - 19wt% and ZnO -- 5 - 50wt% -- desirable -- 7 - 43wt% -- it is desirable to use the glass to contain. such glass -- setting -- further -- aluminum₂O₃ And/or, SiO₂ the content when containing and containing these things -- aluminum₂O₃ less than [20wt%] -- desirable -- 0.1 - 5wt% and SiO₂ It is good less than [9wt%] and to consider as 2 - 7wt% preferably.

[0029] Before sintering, such a ceramic ingredient of a dielectric adds a vehicle and let it be a slurry. As a vehicle, solvents, such as binders, such as ethyl cellulose, a polyvinyl butyral, methacrylic resin, and butyl methacrylate, a terpeneol, butyl carbitol, butyl carbitol acetate, acetate, toluene, alcohol, and a xylene, other various dispersants, an activator, a plasticizer, etc. are mentioned, and the thing of arbitration is suitably chosen according to the purpose among these. As for the addition of a vehicle, it is desirable to consider as about 65-85wt% to the total quantity 100 weight section of the oxide aggregate and glass.

[0030] As an inner conductor, especially for a limit, although there is nothing, the conductivity in a direct current of an inner conductor layer is 1×10^5 . It is desirable to use 1 more than [$\omega^{-1} \text{ cm to}$] conductor material. Moreover, although there is especially no limit in the upper limit of conductivity, it is usually 6.2×10^5 . It is about [$\omega^{-1} \text{ cm to} / 1$].

[0031] Specifically, it is desirable to use silver ($6.17 \times 10^5 \omega^{-1} \text{ cm}^{-1}$) and copper ($5.81 \times 10^5 \omega^{-1} \text{ cm}^{-1}$). In a more desirable mode, the melting point uses the silver near 960 degree C, or the copper near the melting point of 1060 degrees C. Under the present circumstances, it is desirable that the content of silver or copper uses the virgin silver or the pure copper beyond 99.9wt% for the thing beyond 90wt% especially more than purity 99wt%, and a pan. Thus, by using especially virgin silver thru/or a pure copper, the specific resistance and loss which are the inverse number of conductivity can be made very small, and the Q value of a resonator can be raised.

[0032] Therefore, in the case of silver, it is 960 degrees C or more in temperature

which is the melting point, and it is desirable to calcinate at the temperature beyond the sintering termination temperature of a ceramic ingredient, and it is desirable to usually consider as the temperature of 1150-1750 degrees C and further 1200-1700 degrees C. Moreover, in the case of copper, it is 1060 degrees C or more in temperature which is the melting point, and it is desirable to calcinate at the temperature beyond the sintering termination temperature of a ceramic ingredient, and it is desirable to usually consider as the temperature of 1150-1750 degrees C and further 1200-1700 degrees C like the case where it is silver.

[0033] The efficiency of this invention appears by carrying out coincidence baking with ceramic ingredient layers, such as a green sheet, with such a burning temperature. If burning temperature becomes under the melting point and, as for this, becomes low too much, the efficiency of this invention will not appear, but if too high, an inner conductor will disappear by evaporation. As for baking, in the case of silver, it is usually desirable to carry out about 5 to 20 minutes more preferably at the above-mentioned temperature in air for 1 minute to about 1 hour. Moreover, in the case of copper, it is usually 10⁻⁶atm about oxygen tension. It carries out by controlling below. In addition, baking may be performed two or more times and it considers as baking more than the melting point with which are satisfied of the above-mentioned conditions once [at least] then.

[0034] Although approaches, such as inserting the silver foil of a predetermined configuration etc. into a dielectric green sheet, or performing printing or an imprint of conductive paste as the formation approach of an inner conductor pattern, are mentioned, especially print processes are desirable.

[0035] the mean particle diameter (diameter of a major axis when there is an anisotropy) of conducting powder, such as silver dust used when forming a pattern with conductive paste, and copper powder, -- 0.5-20 micrometers extent -
- more -- desirable -- 1-5 micrometers ** -- carrying out is desirable. If dispersibility cannot worsen, the content of the conducting powder in conductive paste cannot be made [many], if particle size is too small, and a content is

made [many], viscosity becomes high and it becomes impossible to form a precise pattern. On the other hand, if particle size is too large, formation of the pattern by screen-stencil, a replica method, etc. will become difficult. Moreover, although there is especially no constraint in the configuration of silver dust, generally it supposes that it is spherical and is good also considering the part or all as a scale-like thing.

[0036] As for especially the content of the conducting powder under inner conductor paste, considering as 70 - 90wt% is desirable 60 - 95wt%. If there are few contents, specific resistance decreases, Q value falls, some patterns after baking are disconnected or specific resistance and Q value vary. Moreover, if too large, the viscosity of a paste will increase and pattern formation will become difficult.

[0037] Moreover, it is desirable to add the glass frit which may add a glass frit for the paste of an inner conductor, and has softening temperature especially near the conducting powder melting point. By adding such a glass frit, generating of the network structure after melting can decrease and the variation in Q value can be suppressed.

[0038] Especially addition of a glass frit is effective, when the conductor material of impalpable powder with small mean particle diameter is used and diffusion of an inner conductor ingredient is prevented, in the conductor material of a major diameter, diffusion does not pose a problem so much, but addition of a glass frit has comparatively desirable how to bend in this case. The direction which does not add a glass frit can reduce loss of the transmission line further.

[0039] When adding the glass frit under inner conductor paste, further 3 - 8wt% of the content is desirable a 10wt% less or equal, especially 1 - 10wt%. Moreover, as for especially a glass frit especially, it is desirable [4 - 6wt% / in a volume ratio] a 10wt% less or equal, especially 2 - 10wt% to conducting powder 5-10 volume % To be contained in two to 30 volume % and a pan below 30 volume %.

[0040] Conducting powder, such as silver dust, and a vehicle besides a glass frit are contained in an inner conductor paste. As a vehicle, solvents, such as

binders, such as ethyl cellulose, a polyvinyl butyral, methacrylic resin, and butyl methacrylate, a terpeneol, butyl carbitol, butyl carbitol acetate, toluene, alcohol, and a xylene, other various dispersants, an activator, a plasticizer, etc. are mentioned, and the thing of arbitration is suitably chosen according to the purpose among these. As for the addition of a vehicle, considering as about 10-20wt% is desirable during a paste.

[0041] The membrane formation approach of an inner conductor paste should just be based on well-known screen printing, a replica method, etc.

[0042] Moreover, this invention forms an inner conductor from at least two sorts of ingredients with which the melting points differ, it is more than the melting point of a low-melt point inner conductor among inner conductors, and moreover is the temperature of under the melting point of a high-melting inner conductor, and may calcinate it at the temperature beyond the sintering termination temperature of a ceramic ingredient.

[0043] As a low-melt point inner conductor in this case, it is desirable to use the above-mentioned silver and copper, and the same effectiveness as the above is acquired.

[0044] What is necessary is on the other hand, just to use a conductor with the melting point higher than the conductor used for a low-melt point inner conductor as a conductor used for a high-melting inner conductor. However, since it calcinates at the middle temperature of the melting point of each a low-melt point and high-melting inner conductor, in order to calcinate both good, as for especially the melting point of the conductor used for a high-melting inner conductor, it is desirable that 30 degrees C or more are 50-200 degrees C and what is high further 50-100 degrees C to the melting point of a low-melt point inner conductor. In addition, since this can also be made to alloy as a high-melting inner conductor using two sorts of metal powders, for example, Ag powder, and Pd powder like the after-mentioned, without performing melting of Ag on the occasion of baking, at this time, that melting point is the melting point of an alloy.

[0045] As a conductor used for such a high-melting inner conductor, when using silver for the conductor of a low-melt point point inner conductor, less than [30wt%] and the Ag-Pd alloy which contains 5 - 10wt% Pd especially are suitable. In this case, Ag powder and Pd powder may be mixed and used instead of using an alloy. If homogeneity is made to distribute these, on the occasion of baking, alloying with Ag and Pd will progress first, and Ag will not fuse. As opposed to silver In addition, less than [100wt%], less than [Ag-Au alloy;20wt%] which contains 50 - 60wt% Au especially, The Ag-Pt alloy which contains 5 - 10wt% Pt especially; Less than [20wt%], The Au-Pd alloy which contains 5 - 20wt% Pd especially; Less than [10wt%], Au-Pt alloy; which contains 5 - 10wt% Pt especially -- golden; -- copper; -- Au-Cu alloy; containing Au not more than 25wt% -- Au-Cu alloy; containing Cu not more than 20wt% -- less than [10wt%] -- The Cu-Pt alloy which contains Pt not more than 5wt% especially; less than [25wt%], the Cu-nickel alloy which contains nickel not more than 10wt% especially are usable. When using copper for a low-melt point point inner conductor furthermore, 7 - 30wt%, and Ag-Pt alloy;2 which contains 10 - 20wt% Pt especially - 20wt %, An Au-Pd alloy, 2 - 20wt% which contains 2 - 10wt% Pd especially, The Au-Pt alloy which contains 2 - 10wt% Pt especially; less than [30wt%], less than [Cu-Pt alloy;40wt%] which contains 15 - 20wt% Pt especially, the Cu-nickel alloy which contains 20 - 30wt% nickel especially are usable.

[0046] In addition, two or more sorts may be used as a high-melting inner conductor, and two or more sorts of low-melt point point inner conductors may be used depending on the case. Moreover, a high-melting inner conductor may fuse a part of the component. However, a low-melt point point inner conductor fuses the all substantially.

[0047] The detail of the inner conductor ingredient at the time of carrying out coincidence baking at the temperature more than the melting point of the above inner conductor ingredients is indicated by Japanese Patent Application No. No. 134199 [four to] by these people, and Japanese Patent Application No. No.

146478 [four to].

[0048] Moreover, in this invention, depending on the ceramic ingredient or conductor material to be used, the oxygen tension of a firing environments may be made lower than the oxygen tension in atmospheric air, and may be performed. For example, when using the ceramic ingredient which added the above glass, using silver as a conductor material, it is 5×10^{-2} atm about oxygen tension. Considering as the following is desirable. Silver lamination, as a result disappearance can be prevented by this, and Q value as a resonator can be made high. However, in order to enable sintering of the glass component of a ceramic ingredient, the lower limit of oxygen tension is 5×10^{-5} atm. It carries out.

[0049] Furthermore, in case silver is used especially as an inner conductor ingredient, it is 1×10^{-1} atm about the oxygen tension at the time of baking. It is 5×10^{-2} atm more preferably hereafter. It is 1×10^{-2} atm especially hereafter.

Considering as the following may be desirable. In case a laminating is carried out to a dielectric ceramic ingredient layer and it calcinates, using silver as an inner conductor ingredient, it is known that silver will dissolve the oxygen in an ambient atmosphere at the time of melting. The oxygen which dissolved to silver at this time is emitted as oxygen gas at the time of cooling solidification of melting silver. This emission oxygen gas becomes the cause of raising the internal pressure between the dielectric ceramic layers which adjoin an inner conductor layer.

[0050] Although it is rare for a problem to arise substantially since the mechanical strength which a dielectric ceramic layer has is also comparatively high when the thickness of said adjoining dielectric ceramic layer is thick at this time, the rise of the internal pressure by generating of emission oxygen gas becomes a cause, and between an inner conductor and a dielectric ceramic ingredient layer, an opening may be generated and it may become the cause of a fall of the Q value of a resonator.

[0051] On the other hand, it has a dielectric ceramic layer in the outermost layer of the direction of a laminating at the time of baking. The distance (t and/or t' which are illustrated to drawing 4) from the front face by the side of said

outermost layer of an inner conductor layer to said outermost layer front face It is 500 micrometers after baking. The following and 300 more micrometers It is especially 200 micrometers hereafter. When it is the following, the rise of the internal pressure between the dielectric ceramic layers which adjoin the inner conductor layer by said emitted oxygen gas by the cause It is easy to cause the accident on which the adjoining dielectric ceramic layer and an inner conductor layer exfoliate. In this case, there is a dielectric ceramic layer of the outermost layer of the direction of a laminating which is the part which exfoliation accident tends to generate two direction upper and lower sides of a laminating. Among these, when the distance from the front face by the side of the outermost layer of one [at least] inner conductor layer to an outermost layer front face is said following, it is easy to cause the accident by exfoliation. In addition, the thickness of said dielectric ceramic layer is usually 40 micrometers. It is used above.

[0052] In such a case, it is said 1×10^{-1} atm about the oxygen tension at the time of baking. It is 5×10^{-2} atm more preferably hereafter. It is 1×10^{-2} atm especially hereafter. Considering as the following is desirable. namely,, so that the thickness of said dielectric ceramic ingredient layer which is in the outermost layer of the direction of a laminating at the time of baking is thin -- silver -- since it is easy to generate exfoliation in response to the effect of the internal pressure rise between the conductors and dielectric ceramic layers by the oxygen gas emitted at the time of cooling solidification of a conductor, it is so desirable that the thickness of a dielectric ceramic ingredient layer is thin to make low the oxygen tension at the time of baking.

[0053] However, the inside of the dielectric ceramic ingredient described above when the oxygen tension at the time of baking was made low, CaO-MgO-TiO₂ A system and BaO-TiO₂-SnO₂ System, A BaO-Nd₂ O₃-TiO₂-Bi₂ O₃-aluminum₂ O₃-MnO system, ZrO₂-SnO₂-TiO₂ A system and SrO-ZrO₂-TiO₂ System, BaO-Sm₂ O₅-TiO₂ A system and PbO-BaO-Nd₂ O₃-TiO₂ A system and Li₂ O-Na₂ O-Sm₂O₅-TiO₂ For a system etc., the oxygen tension at the time of baking is 1×10^{-4} atm. Below, it becomes that it is easy to be returned. When components, such

as a resonator, are constituted when the dielectric ceramic ingredient was returned for example, the Q value will fall remarkably. For this reason, the dielectric ceramic ingredient of these presentations is used and the distance of the outermost layer front face of the direction of a laminating and the front face by the side of the outermost layer of an inner conductor layer is said 500 micrometers further at the time of baking. The multilayer ceramic components with the following configurations 1×10^{-4} atm It exceeds and is 1×10^{-1} atm. They are 5×10^{-2} - 1×10^{-3} atm, especially 1×10^{-2} - 1×10^{-3} atm more preferably hereafter. Calcinating under oxygen tension is desirable.

[0054] Moreover, when using especially copper as conductor material, it is usually 1×10^{-6} atm about oxygen tension as mentioned above. It carries out by controlling below. When oxygen tension is too high, an internal electrode may disappear by copper oxidation.

[0055] However, there is an ingredient which will be returned as mentioned above if oxygen tension is reduced depending on a dielectric ceramic ingredient. For this reason, when using copper for an inner conductor, it is desirable to use the ingredient which is hard to be returned even if it reduces oxygen tension. As such an ingredient, it is MgO-SiO₂. A system and BaO-MgO-CoO-Nb₂O₅ A system and PbO-CaO-ZrO₂ A system etc. is mentioned.

[0056] The multilayer ceramic components of this invention have the high Q value as a resonator, and about 280 to 430 Q value is obtained on conditions with a thickness [of a dielectric] of 3mm.

[0057] As multilayer ceramic components of this invention, for example, a laminating mold filter may be the thing of a configuration of being shown in drawing 2 .

[0058] The filter 1 shown in drawing 2 is a two-step filter, and inner conductors 21, 22, and 23 are put in the element assembly 11 of a dielectric ceramic ingredient in between like illustration.

[0059] Moreover, you may be the thing of a configuration of being shown in drawing 3 , and a filter 2 is put in between in the element assembly 11 of a

dielectric ceramic ingredient by juxtaposition like illustration of inner conductors 25 and 26.

[0060] In addition, the outside surface is covered with the metal or the insulating material also in which filter of drawing 2 and drawing 3 .

[0061] Furthermore, you may be the thing of a configuration of being shown in drawing 4 . In drawing 4 , it has a dielectric ceramic layer in the outermost layer of the direction of a laminating, and the inner conductor layers 27 and 29 are 500 micrometers from the outermost layer front face of said direction of a laminating. It is arranged at the following distance. Thus, at least one side of thickness t of the dielectric ceramic layer of the outermost layer or t' is 500 micrometers after baking. It is the following, and when using silver for the inner conductor layer 27 or 29 further, the dielectric ceramic layer of the outermost layer becomes easy to exfoliate with the inner conductor layer 27 or 29 as mentioned above. In addition, with the filter shown in drawing 4 , since the inner conductor layers 27 and 29 function as a shielding layer, an external electrode is not usually prepared in an outside surface.

[0062] Such a laminating mold filter casts a green sheet with a doctor blade method etc. using the temporary-quenching powder of a dielectric ceramic ingredient, it carries out the laminating of the sheet which printed the paste of an inner conductor ingredient with screen printing etc. to it, and printed it by the predetermined pattern to it, and it carries out thermocompression bonding with a heat press, and it is the temperature more than the melting point of an inner conductor after a debinder, and can be calcinated and obtained at the temperature beyond the sintering termination temperature of a ceramic ingredient. Then, what is necessary is to print the paste for external electrodes if needed, and just to carry out it being burned and carrying out an external electrode etc. In addition, it is good also by the printing lamination.

[0063] Thus, the thickness of the whole dielectric of the laminating mold filter obtained is about 0.5-4mm. Moreover, the thickness of an inner conductor is 20-100 micrometers. Extent and width of face are about 0.5-2mm. 50 micrometers in

under the present circumstances, thickness The following and 40 more micrometers The effectiveness of this invention is doubled at the following times. Moreover, the thickness of a dielectric ceramic layer is 40-150 micrometers. It is extent. In addition, the multilayer ceramic components of this invention are usually 200MHz. It is 800MHz - 10GHz especially above. It is used in the frequency band of extent.

[0064]

[Example] Hereafter, an example explains this invention concretely.

[0065] By each presentation shown in example 1 table 1, it is 150-200 micrometers after temporary quenching, grinding, and slurry preparation and by the doctor blade method. A green sheet is cast. Carry out laminating thermocompression bonding of the sheet which screen-stenciled Ag conductive paste and was printed to it, calcinate after a debinder on the conditions shown in Table 1, make an external electrode this baking object with silver baking after printing the paste for external electrodes, and it sets to drawing 2 . 1 / 4lambda resonator (sample A-I) which made the resonator one step were produced respectively (Table 1). The number of laminatings at this time was made into 20 layers.

[0066] It sets to 1 / 4lambda resonator, and the thickness of an inner conductor is 60 micrometers. Width of face was 2mm.

[0067] Moreover, thickness of a dielectric was set to 3.0mm as shown in Table 1.

[0068] The whole dimension was set to 1/4lambda(1/4 of wavelength lambda in dielectric) x5mmx3.0mm.

[0069] In addition, Ag conductive paste used in the above carries out mixed distribution with 3 rolls, and obtains the thing of the presentation shown below. In addition, the melting point and the conductivity of Ag are shown in Table 1.

[0070]

Silver dust (mean-diameter 3micrometer : 99.9% or more of purity) 90wt% Acrylic resin (binder) 2.5wt% Terpeneol (solvent) 7.5wt% [0071] Furthermore, YHP8510 network analyzer estimated the filter shape of 1 / 4lambda resonator produced as

mentioned above, and it calculated the Q value as a resonator. A result is shown in Table 1.

[0072] In addition, production of the green sheet of the dielectric ceramic ingredient in the above was performed according to the approach of Japanese Patent Application No. No. 327352 [three to] by JP,47-21698,A, JP,52-118599,A, JP,61-72676,A, JP,4-32483,B, and these people etc. The temporary-quenching conditions in that case were carried out as shown in Table 2.

[0073] Moreover, in the above, instead of producing a green sheet, it cast in the shape of a cylinder, and calcinated as baking conditions shown in Table 2, and the sample was obtained (sample No.1-8). After processing these samples into 10mm phix5mm, a dielectric constant (epsilon), and Q and f value were calculated with the dielectric resonance method. Moreover, it asked for the slope of a line which connected the resonance frequency of -40 degrees C, and the resonance frequency of 80 degrees C, and the resonance frequency temperature coefficient (tauf) was computed. The result was shown in Table 2.

[0074] Furthermore, about each ingredient, sintering termination temperature (degree C) and sintering initiation temperature (degree C) were searched for from the heat shrink curve in the programming rate of 200 degrees C/hour, and it was shown in Table 3.

[0075]

[Table 1]

表 1

サンプル	誘電体セラミック材料 組成	材料	導体材料 熔点 導電率 ($\Omega^{-1}\text{cm}^{-1}$)	焼成条件 温度 時間 雰囲気	共振器特性 Q値	誘電体 厚さ
A	2MgO·SiO ₂ -CaTiO ₃ -SrTiO ₃ (90 \pm 1%) (2 \pm 1%) (8 \pm 1%) -MgO - La ₂ O ₃ (1.5wt%) (1.5wt%)	Ag	960℃ 6.17 \times 10 ⁵	1230℃ 10分 大気中	338	3mm
B	MgTiO ₃ -TiO ₂ -CaTiO ₃ (90 \pm 1%) (10 \pm 1%) (6.2wt%)	Ag	960℃ 6.17 \times 10 ⁵	1380℃ 10分 大気中	418	3mm
C	BaO - CoO - MgO - Nb ₂ O ₅ (58.8wt%) (4.8wt%) (2.6wt%) (33.8wt%)	Ag	960℃ 6.17 \times 10 ⁵	1470℃ 10分 大気中	390	3mm
D	BaO·x [(1-y)TiO ₂ ·ySnO ₂] (x=4.4, y=0.09)	Ag	960℃ 6.17 \times 10 ⁵	1360℃ 10分 大気中	316	3mm
E	BaO - TiO ₂ - Nd ₂ O ₃ (14.7 \pm 1%) (70.0 \pm 1%) (15.3 \pm 1%) - Bi ₂ O ₃ - Al ₂ O ₃ - MnO (7.5wt%) (1.0wt%) (0.1wt%)	Ag	960℃ 6.17 \times 10 ⁵	1320℃ 10分 大気中	322	3mm
F	BaO·x [(1-y)TiO ₂ ·ySnO ₂] (x=4.4, y=0.09)	Ag	960℃ 6.17 \times 10 ⁵	1360℃ 10分 1 \times 10 ⁻³ 気圧 (0.2分圧)	368	3mm
G	Ba(Mg _{1/3} Ta _{2/3})O ₃	Ag	960℃ 6.17 \times 10 ⁵	1670℃ 10分 大気中	420	3mm
H	(Zr _{0.8} Sn _{0.2})TiO ₄	Ag	960℃ 6.17 \times 10 ⁵	1600℃ 10分 大気中	388	3mm
I	(Pb _{0.8} Ca _{0.2})ZrO ₃	Ag	960℃ 6.17 \times 10 ⁵	1450℃ 10分 大気中	300	3mm

[0076]

[Table 2]

表 2

サンプル No.	誘電体セラミックス材料 組成	仮焼条件 温度 時間 (°C)	焼成条件 温度 時間 (°C)	ε	$Q \cdot f$ (GHz)	τf (ppm/°C)
1	2MgO·SiO ₂ -CaTiO ₃ -SrTiO ₃ (90±1%) (2±1%) (8±1%) -MgO - La ₂ O ₃ (1.5wt%) (1.5wt%)	1000 2時間	1230 10分	7	13000	0
2	MgTiO ₃ -TiO ₂ -CaTiO ₃ (90±1%) (10±1%) (6.2wt%)	1100 3時間	1380 10分	20	40500	0
3	BaO - CoO - MgO - Nb ₂ O ₅ (58.8wt%) (4.8wt%) (2.6wt%) (33.8wt%)	1200 2時間	1470 10分	33	70000	-4.0
4	BaO·x [(1-y)TiO ₂ ·ySnO ₂] (x=4.4, y=0.09)	1100 2時間	1360 10分	37	35000	+4.0
5	BaO - TiO ₂ - Nd ₂ O ₃ (14.7±1%) (70.0±1%) (15.3±1%) - Bi ₂ O ₃ - Al ₂ O ₃ - MnO (7.5wt%) (1.0wt%) (0.1wt%)	1200 2時間	1320 10分	93	4000	+8.0
6	Ba(Mg _{1/3} Ta _{2/3})O ₃	1300 2時間	1670 10分	21	220000	+4.0
7	(Zr _{0.8} Sn _{0.2})TiO ₄	1200 2時間	1600 10分	38	55000	0
8	(Pb _{0.85} Ca _{0.15})ZrO ₃	1000 2時間	1450 10分	110	3300	+13

[0077]

[Table 3]

表 3

サンプル No.	誘電体セラミック材料 組 成	焼結終了温度 (昇温速度：200℃/hr)	焼結開始温度
1	2MgO·SiO ₂ -CaTiO ₃ -SrTiO ₃ (90モル%) (2モル%) (8モル%) -MgO - La ₂ O ₃ (1.5wt%) (1.5wt%)	1226℃	1141℃
2	MgTiO ₃ -TiO ₂ - CaTiO ₃ (90モル%) (10モル%) (6.2wt%)	1357℃	1179℃
3	BaO - CoO - MgO - Nb ₂ O ₅ (58.8wt%) (4.8wt%) (2.6wt%) (33.8wt%)	1468℃	1306℃
4	BaO·x [(1-y)TiO ₂ ·ySnO ₂] (x=4.4, y=0.09)	1307℃	1172℃
5	BaO - TiO ₂ - Nd ₂ O ₃ (14.7モル%) (70.0モル%) (15.3モル%) - Bi ₂ O ₃ - Al ₂ O ₃ - MnO (7.5wt%) (1.0wt%) (0.1wt%)	1282℃	1154℃
6	Ba(Mg _{1/3} Ta _{2/3})O ₃	1652℃	1523℃
7	(Zr _{0.8} Sn _{0.2})TiO ₄	1580℃	1445℃
8	(Pb _{0.8} Ca _{0.2})ZrO ₃	1427℃	1281℃

[0078] 1 / 4lambda resonator of this invention show high Q value so that clearly from the result of Table 1. when carrying out coincidence baking of a dielectric ceramic ingredient and the conductor material and producing a laminating filter conventionally, it is necessary to calcinate at the temperature which does not fuse an inner conductor ingredient, and a thing for elevated-temperature baking which is used above presupposes that it cannot use -- having -- **** (JP,3-290358,A etc.) -- the fact which reverses this became clear.

[0079] When the ceramic ingredient for low-temperature baking (the sintering termination temperature in the programming rate of 200 degrees C/hour is presumed to be 925 degrees C or less.) indicated by the JP,3-295856,A example 6 was actually used, and also $1/4\lambda$ resonator was similarly produced like the above and Q value was calculated, it turned out that Q value clearly lower than the thing of this invention is shown.

[0080] The resonator with the configuration of drawing 4 was calcinated like the example 1 using the presentation of Samples E, H, and I shown in example 2 table 1. However, thickness [of the surface dielectric ceramic ingredient layer which makes a firing environments each condition which shows oxygen tension in Table 4, and is shown in drawing 4] t, and t' is 200 micrometers after baking. As it became, sample No.21-24, 31-34, and 41-46 were produced.

[0081] Furthermore, a firing environments is 400 micrometers after baking using the presentation of Sample E about thickness [of the dielectric ceramic ingredient layer of the direction surface of a laminating which makes the conditions which show oxygen tension in Table 4, and is shown in drawing 4] t, and t'. As it became, it reached sample No.25, and 26 was produced.

[0082] The exfoliation situation of the dielectric ceramic ingredient layer of the direction surface of a laminating of each obtained baking object was evaluated, and the result was shown in Table 4.

[0083] Subsequently, $1/4\lambda$ resonator was produced about the sample in which exfoliation was not accepted. The number of laminatings at this time was made into 20 layers among inner conductors 27 and 29. It sets to $1/4\lambda$ resonator, and the thickness of an inner conductor 28 is 60 micrometers. Width of face was 2mm. Moreover, thickness of the dielectric of a resonator part was set to 3.0mm as shown in Table 1. The dimension of the whole resonator part was set to $1/4\lambda$ (1/4 of wavelength λ in dielectric) x5mmx3.0mm.

[0084] The filter shape of each obtained resonator was measured like the example 1, and the result was shown in Table 4. Moreover, the data of the Q value of the resonator of a baking-among atmospheric air sample (No.21, 25, 31

and 41) with which exfoliation was accepted described the thing of the same dielectric ceramic ingredient of Table 1 in Table 4.

[0085]

[Table 4]

表 4

サンプル No.	誘電体セラミック材料組成	内部導体 材料	焼成雰囲気 (酸素分圧) (atm)	内部導体と誘電体 セラミック材料層 との剥離の有無	共振器特性 Q値	セラミック 材料層厚さ t (μm)
2 1 (比較)	BaO -TiO ₂ -Nd ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (1.0wt%) (0.1wt%)	Ag	大気中	剥離発生	322	200
2 2	BaO -TiO ₂ -Nd ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (1.0wt%) (0.1wt%)	Ag	1×10^{-2}	剥離なし	320	200
2 3	BaO -TiO ₂ -Nd ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (1.0wt%) (0.1wt%)	Ag	1×10^{-3}	剥離なし	306	200
2 4 (比較)	BaO -TiO ₂ -Nd ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (1.0wt%) (0.1wt%)	Ag	1×10^{-4}	剥離なし	161	200
2 5 (比較)	BaO -TiO ₂ -Nd ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (1.0wt%) (0.1wt%)	Ag	大気中	剥離発生	322	400
2 6	BaO -TiO ₂ -Nd ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (1.0wt%) (0.1wt%)	Ag	1×10^{-2}	剥離なし	318	400
3 1 (比較)	(Zr _{0.8} Sn _{0.2})TiO ₄	Ag	大気中	剥離発生	338	200
3 2	(Zr _{0.8} Sn _{0.2})TiO ₄	Ag	1×10^{-2}	剥離なし	384	200
3 3	(Zr _{0.8} Sn _{0.2})TiO ₄	Ag	1×10^{-3}	剥離なし	352	200
3 4 (比較)	(Zr _{0.8} Sn _{0.2})TiO ₄	Ag	1×10^{-4}	剥離なし	140	200
4 1 (比較)	(Pb _{0.88} Ca _{0.12})ZrO ₃	Ag	大気中	剥離発生	300	200
4 2	(Pb _{0.88} Ca _{0.12})ZrO ₃	Ag	1×10^{-2}	剥離なし	310	200
4 3	(Pb _{0.88} Ca _{0.12})ZrO ₃	Ag	1×10^{-3}	剥離なし	298	200
4 4	(Pb _{0.88} Ca _{0.12})ZrO ₃	Ag	1×10^{-4}	剥離なし	292	200
4 5	(Pb _{0.88} Ca _{0.12})ZrO ₃	Ag	1×10^{-6}	剥離なし	288	200
4 6	(Pb _{0.88} Ca _{0.12})ZrO ₃	Ag	1×10^{-6}	剥離なし	281	200

[0086] If there is no generating of exfoliation of the oxygen tension of a firing environments in the range of this invention and the oxygen tension of a firing environments is made into the inside of atmospheric air so that clearly from the result of Table 4, exfoliation will have occurred. Moreover, if the oxygen tension of a firing environments is set to 1×10^{-4} , the property of a resonator will fall in the example using Samples E and H as a dielectric ceramic ingredient. On the other hand, in the example using Sample I as a dielectric ceramic ingredient, even if the oxygen tension of a firing environments is 1×10^{-6} , the fall of the property of a resonator is not accepted.

[0087] In addition, the sintering termination temperature T20 of the dielectric ceramic ingredient in above-mentioned this invention All are temperature with a melting point [of Ag] of +150 degrees C or more. Moreover, it was checked that temperature T20' (drawing 1 : point G) which is equivalent to 80% of place from Point C in the distance of the sintering initiation temperature (drawing 1 : point C) and the sintering termination temperature T20 (drawing 1 R> 1: point F) which were searched for from the heat shrink curve is temperature with a melting point [of Ag] of +50 degrees C or more.

[0088] As an example 3 dielectric ceramic ingredient, using the samples A, D, and E shown in Table 1, the green sheet was cast by each presentation like the example 1, and the straight-line pattern was printed with screen printing using the same Ag conductive paste as an example 1 to it. Laminating thermocompression bonding of the green sheet of the dielectric ceramic ingredient same further respectively on the printed sheet was carried out, the oxygen tension behind a debinder and in a firing environments was set to 1×10^{-2} , and others were calcinated according to the baking conditions of each dielectric ceramic ingredient shown in Table 1, and acquired the baking object.

[0089] The size of a baking object is 400 micrometers in 56mm long, 65mm wide, and thickness. It carried out. moreover, Ag -- a conductor -- a baking object

lengthwise direction -- 24 per 1 baking object -- almost -- regular intervals -- arranging -- each straight-line pattern of a conductor -- the size after baking -- about 40 micrometers in die length of about 46mm, 1mm of ****, and thickness It printed so that it might become. In addition, the printing location of a conductor was made into the location which is not exposed to the laminating backward exterior.

[0090] observation place each acquired baking object (ten per dielectric ceramic ingredient 1 presentation were produced) on a transparence glass plate, irradiate the source of the light from the glass plate lower part, and according the transmitted light to viewing, and observation of the transparency X-ray image by the conventional method -- carrying out -- Ag -- the existence of the open-circuit part of a conductor was investigated. Consequently, the open-circuit part was 5-10 per 1 baking object about the sample of each dielectric ceramic ingredient.

[0091] As an example of comparison 1 dielectric ceramic ingredient, it is the mean particle diameter of about 1 micrometer. It used in the end of alumimium nitride powder, the calcium carbonate of the amount which becomes 0.5wt(s)% by CaO conversion as sintering acid further was added, and the green sheet was created as a slurry with the binder etc. Using Ag conductive paste, the same pattern as an example 3 was printed similarly, laminating thermocompression bonding of the still more nearly same green sheet was carried out, after the debinder, in nitrogen-gas-atmosphere mind, the temperature of 1600 degrees C, it calcinated for 10 minutes and the baking object was acquired. In addition, the size of a baking object or a conductor, a pattern, the printing position of a conductor, etc. presupposed that it is the same as an example 3.

[0092] ten acquired baking objects -- an example 3 -- the same -- carrying out -- Ag -- the existence of the open-circuit part of a conductor was investigated. Consequently, although an open-circuit part is 40-50 per 1 baking object and it did not result to the open circuit further, many parts the width of face of a conductor carried out [parts] a constriction were accepted.

[0093] When the mixture of an oxide or an oxide is used as a dielectric ceramic

ingredient so that more clearly than an example 3 and the example 1 of a comparison, as compared with the case where wettability bad alumimium nitride with molten metal is used, the disconnection fault incidence rate of a conductor falls greatly.

[0094] Using copper as an example 4 inner-conductor ingredient, using the presentation of the samples A, C, and I of Table 1 as a dielectric ceramic ingredient, oxygen tension was set to 1×10^{-6} as a firing environments, and also the resonator was created like the example 1.

[0095] In addition, used Cu conductive paste carries out mixed distribution with 3 rolls, and obtains the thing of the presentation shown below.

[0096]

Copper powder (mean-diameter 5micrometer : 99.9% or more of purity) 90wt%
Acrylic resin (binder) 2.5wt% Terpeneol (solvent) 7.5wt% [0097] Each obtained resonator showed the good resonator property (Q value).

[0098]

[Effect of the Invention] According to this invention, the dielectric ceramic ingredient which could carry out eburnation of the inner conductor, and could moreover make front-face nature good, and was excellent in a dielectric constant, dielectric loss (Q-f), etc. can be used, and, as a result, improvement in properties, such as Q value, can be aimed at. Furthermore, generating of generating of the defective by exfoliation with an inner conductor layer and a dielectric ceramic layer, an open circuit of an inner conductor layer, etc. can be decreased at the time of baking.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the graph which shows the heat shrink curve for explaining how searching for sintering termination temperature.

[Drawing 2] It is the outline block diagram showing the laminating mold filter in this invention typically.

[Drawing 3] It is the outline block diagram showing the laminating mold filter in this invention typically.

[Drawing 4] It is the outline block diagram showing the laminating mold filter in this invention typically.

[Description of Notations]

1, 2, 3 Laminating mold filter

11 Element Assembly of Dielectric Ceramic Ingredient

21-23, 25-29 Inner conductor

[Translation done.]

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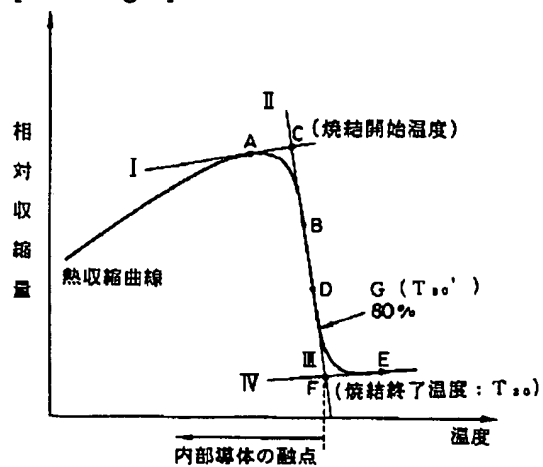
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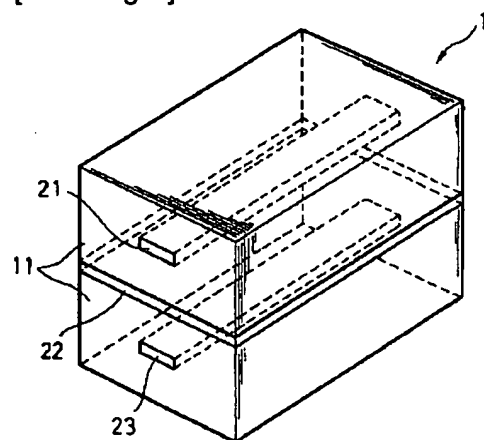
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DRAWINGS

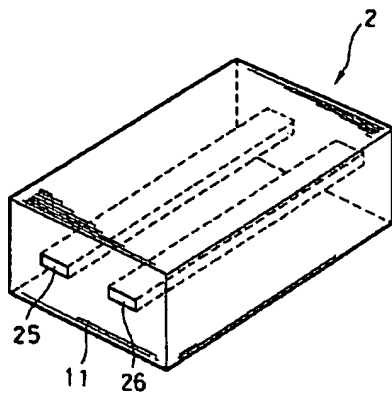
[Drawing 1]



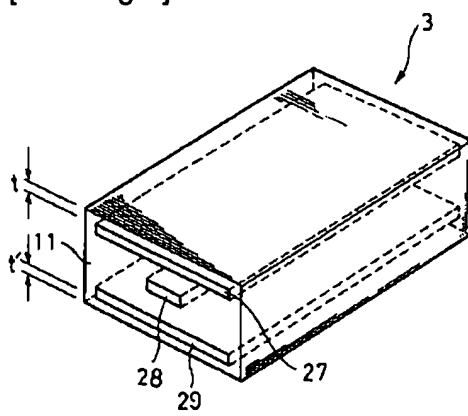
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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(21)出願番号	特願平5-267971	(71)出願人	000003067 ティーディーケイ株式会社 東京都中央区日本橋一丁目13番1号
(22)出願日	平成5年(1993)9月30日	(72)発明者	鈴木 和明 東京都中央区日本橋一丁目13番1号 ティーディーケイ株式会社内
(31)優先権主張番号	特願平4-361377	(72)発明者	古林 真 東京都中央区日本橋一丁目13番1号 ティーディーケイ株式会社内
(32)優先日	平4(1992)12月28日	(72)発明者	三浦 太郎 東京都中央区日本橋一丁目13番1号 ティーディーケイ株式会社内
(33)優先権主張国	日本(JP)	(74)代理人	弁理士 石井 陽一
		最終頁に続く	

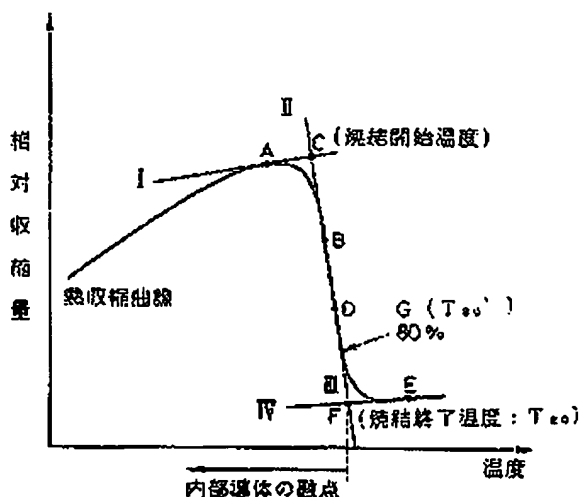
(54)【発明の名称】 多層セラミック部品

(57)【要約】

【目的】 Q値等の特性の向上を図ることができ、さらに、焼成時に内部導体層と誘電体セラミック材料層との剥離による不良品や、内部導体層の断線等の発生が少ない共振器等の多層セラミック部品を提供する。

【構成】 昇温速度200℃/時間における熱収縮曲線から求めた焼結終了温度が内部導体の融点以上沸点以下の温度であり、誘電率および誘電損失(Q・f)に優れた酸化物の誘電体セラミック材料層上に内部導体のパターンを形成し、積層後、内部導体の融点以上の温度で焼成する。このとき内部導体が銀で、最外層に誘電体セラミック層を有し、内部導体の最外層側表面から誘電体セラミック層最外層表面までの距離が500μm以下の場合、あるいは内部導体が銅の場合、雰囲気中の酸素分圧

*図1参照、*図2参照



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【特許請求の範囲】

【請求項1】 内部導体層と複数の誘電体セラミック層とを有する多層セラミック部品であって、昇温速度200℃/時間における熱収縮曲線から求めた焼結終了温度が内部導体の融点以上沸点以下の温度である酸化物の誘電体セラミック材料の誘電体セラミック材料層を用意し、

この誘電体セラミック材料層上に内部導体のパターンを形成し、さらにこれを前記誘電体セラミック材料層と積層し、

前記内部導体の融点以上の温度で焼成して得られた多層セラミック部品。

【請求項2】 前記焼成温度が、前記焼結終了温度以上の温度である請求項1の多層セラミック部品。

【請求項3】 前記誘電体セラミック材料の温度20℃における比誘電率 ϵ が、6.5～120である請求項1または2の多層セラミック部品。

【請求項4】 前記誘電体セラミック材料が、MgO-SiO₂系、CaO-MgO-TiO₂系、BaO-TiO₂-SnO₂系、BaO-MgO-CoO-Nb₂O₅系、BaO-Nd₂O₃-TiO₂-Bi₂O₃-Al₂O₃-MnO系、BaO-MgO-Ta₂O₅系、ZrO₂-SnO₂-TiO₂系、PbO-CaO-ZrO₂系、SrO-ZrO₂-TiO₂系、BaO-Sm₂O₃-TiO₂系、PbO-BaO-Nd₂O₃-TiO₂系およびLi₂O-Na₂O-Sm₂O₃-TiO₂系のいずれかである請求項1～3のいずれかの多層セラミック部品。

【請求項5】 前記内部導体を構成する金属は、銀または銅の含有量が90wt%以上のものである請求項1～4のいずれかの多層セラミック部品。

【請求項6】 前記内部導体を構成する金属が銀であり、 1×10^{-3} atm以下の酸素分圧下で焼成して得られた請求項1～5のいずれかの多層セラミック部品。

【請求項7】 最外層に誘電体セラミック層を有し、前記内部導体層の前記最外層側表面から前記最外層表面までの距離が500μm以下である請求項6の多層セラミック部品。

【請求項8】 前記誘電体セラミック材料が、CaO-MgO-TiO₂系、BaO-TiO₂-SnO₂系、BaO-Nd₂O₃-TiO₂-Bi₂O₃-Al₂O₃-MnO系、BaO-MgO-Ta₂O₅系、ZrO₂-SnO₂-TiO₂系、SrO-ZrO₂-TiO₂系、BaO-Sm₂O₃-TiO₂系、PbO-BaO-Nd₂O₃-TiO₂系およびLi₂O-Na₂O-Sm₂O₃-TiO₂系のいずれかである請求項1～7のいずれかの多層セラミック部品。

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た請求項1～5のいずれかの多層セラミック部品。

【請求項10】 誘電体セラミック材料が、MgO-SiO₂系、BaO-MgO-CoO-Nb₂O₅系およびPbO-CaO-ZrO₂系のいずれかである請求項9の多層セラミック部品。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、主にマイクロ波領域で使用される誘電体共振器やフィルタなどの多層セラミック部品に関する。

【0002】

【従来の技術】多層セラミック部品、例えば誘電体共振器の使用周波数領域が拡大するにつれて、特にマイクロ波領域において使用される誘電体共振器等の小型化が望まれている。このような要請からマイクロ波用誘電体セラミック材料が種々開発されており、特に小型化を實現するものとして高誘電率を示すことが要求される。

【0003】また、共振特性をさらに高いものとするために、マイクロ波に適したAg、Cu等の導体材料を内部電極として用い、セラミック材料を積層する方法が採用されている。共振器等の多層セラミック部品を製作する場合、グリーンシート法や積層印刷法が用いられており、導体材料とセラミック材料とを同時焼成する方法が採用されている。

【0004】従来、このような方法により十分な特性を得るためには、内部導体材料の溶融を防止する必要があると考えられており、内部導体材料の融点以下の温度で焼成する必要があるとされていた。このため、高温で焼成する必要があるセラミック材料は、高誘電特性を示すものであっても使用できないとされていた。この結果、低温焼成可能な誘電体セラミック材料については種々の提案がなされている（特開平3-295854号、特開平3-295855号、特開平3-295856号、特開平3-295858号、特開平3-295859号公報等）。

【0005】しかし、上記の従来法に対し、種々検討を加えたところ、本発明者らは、内部導体材料の融点以上の温度で同時焼成することにより、内部導体が溶融して緻密化し、導体紛によって生じる内部導体内の粒界を實質的に消滅させることができ、共振器としてのQ値を向上するなど、特性の向上を図ることができることを見出し、種々の提案を行なっている（特願平3-306760号、同4-134199号、同4-146478号、同3-360323号、同4-313997号）。

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題があり、この点の改善が望まれている。

【0007】なお、特開平2-197189号公報では、金、銀、銅のうちの1種以上を用いて内部導体を形成した窒化アルミニウム回路基板を焼成することが提案されている。窒化アルミニウム回路基板の最適な焼成温度は、上記内部導体の熔融温度以上であり、これらの内部導体は焼成時に実質的に熔融する。この提案では、窒化アルミニウムのもつ濡れ性の悪さ、緻密化速度の早さ等を利用して、金、銀、銅のような比較的熔融温度の低い内部導体材料を用いても、窒化アルミニウム回路基板に内部配線材料として導体回路を形成することができたとしている。そして、この際、本発明におけると同様の熔融による内部導体の緻密化が生じていると考えられる。

【0008】しかし、例えば共振器等の高周波（例えば200MHz～10GHz程度の周波数）用の多層セラミック部品をこのような窒化アルミニウムを用いて製造した例はない。小型化が望まれている高周波用の部品において、一般に窒化アルミニウムのような比較的誘電率の低い材料は使用しにくく、使用しても大型化してしまう。さらに、窒化アルミニウムは熔融金属に対しての濡れ性が悪い。このため、内部導体の緻密化は生じるが、その界面等には欠陥が生じやすく、はなはだしいときには導体パターンの狭窄や断線が生じる。小型化が求められている高周波用等の部品では、誘電体層の薄層化とともに、内部導体層の厚さや幅も、薄層化、狭小細線化が求められており、特に薄層化、狭小細線化をしようとする場合には内部導体層の断線等の欠陥の発生が顕在化する。

【0009】また、内部導体として特に銀を用い、誘電体セラミック材料として酸化物を用い、さらに内部導体と部品表面との間の誘電体セラミック材料層の厚さが薄い積層複合部品等の焼成に際して、内部導体と誘電体セラミック材料層とが剥離する不良品が多数発生する。

【0010】

【発明が解決しようとする課題】本発明の目的は、誘電率および誘電損失（ $Q \cdot f$ ）に優れた誘電体セラミック材料を用い、かつ内部導体を緻密化し、しかも表面性を良好にすることができる結果、 Q 値等の特性の向上を図ることができる。さらに、焼成時に内部導体層と誘電体セラミック材料層との剥離による不良品や、内部導体層の断線等の発生が少ない多層セラミック部品を提供することにある。

【0011】

（本発明の他の特徴的な事項）とを明らかにする。以下、

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ラミック材料の誘電体セラミック材料層を用意し、この誘電体セラミック材料層上に内部導体のパターンを形成し、さらにこれを前記誘電体セラミック材料層と積層し、前記内部導体の融点以上の温度で焼成して得られた多層セラミック部品。

（2） 前記焼成温度が、前記焼結終了温度以上の温度である上記（1）の多層セラミック部品。

（3） 前記誘電体セラミック材料の温度20℃における比誘電率 ϵ が、6.5～120である上記（1）または（2）の多層セラミック部品。

（4） 前記誘電体セラミック材料が、 $MgO-SiO_2$ 系、 $CaO-MgO-TiO_2$ 系、 $BaO-TiO_2-SnO_2$ 系、 $BaO-MgO-CoO-Nb_2O_5$ 系、 $BaO-Nd_2O_3-TiO_2-Bi_2O_3-Al_2O_3-MnO$ 系、 $BaO-MgO-Ta_2O_5$ 系、 $ZrO_2-SnO_2-TiO_2$ 系、 $PbO-CaO-ZrO_2$ 系、 $SrO-ZrO_2-TiO_2$ 系、 $BaO-Sm_2O_3-TiO_2$ 系、 $PbO-BaO-Nd_2O_3-TiO_2$ 系および $Li_2O-Na_2O-Sm_2O_3-TiO_2$ 系のいずれかである上記（1）～（3）のいずれかの多層セラミック部品。

（5） 前記内部導体を構成する金属は、銀または銅の含有量が90wt%以上のものである上記（1）～（4）のいずれかの多層セラミック部品。

（6） 前記内部導体を構成する金属が銀であり、 $1 \times 10^{-1} atm$ 以下の酸素分圧下で焼成して得られた上記（1）～（5）のいずれかの多層セラミック部品。

（7） 最外層に誘電体セラミック層を有し、前記内部導体層の前記最外層側表面から前記最外層表面までの距離が500 μm 以下である上記（6）の多層セラミック部品。

（8） 前記誘電体セラミック材料が、 $CaO-MgO-TiO_2$ 系、 $BaO-TiO_2-SnO_2$ 系、 $BaO-Nd_2O_3-TiO_2-Bi_2O_3-Al_2O_3-MnO$ 系、 $BaO-MgO-Ta_2O_5$ 系、 $ZrO_2-SnO_2-TiO_2$ 系、 $SrO-ZrO_2-TiO_2$ 系、 $BaO-Sm_2O_3-TiO_2$ 系、 $PbO-BaO-Nd_2O_3-TiO_2$ 系および $Li_2O-Na_2O-Sm_2O_3-TiO_2$ 系、のいずれかであり、 $1 \times 10^{-1} atm$ を超え、 $1 \times 10^{-1} atm$ 以下の酸素分圧下で焼成して得られた上記（6）または（7）の多層セラミック部品。

（9） 前記内部導体を構成する金属が銅であり、 $1 \times 10^{-1} atm$ 以下の酸素分圧下で焼成して得られた上記（1）～（5）のいずれかの多層セラミック部品。

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【具体的構成】以下、本発明の具体的構成について詳細に説明する。

【0013】本発明の多層セラミック部品は、誘電体セラミック材料のグリーンシート上に内部導体パターンを形成した後、このグリーンシートを積層して、熱プレスにて圧着し、その後焼成して製造される。このようないわゆるグリーンシート法他、誘電体のペーストと内部導体のペーストとを交互に積層するいわゆる印刷積層法を用いてもよい。

【0014】この場合、本発明では、昇温速度200℃/時間における熱収縮曲線から求めた焼結終了温度が内部導体の融点以上沸点以下の温度である誘電体セラミック材料を用い、内部導体の融点以上の温度で焼成している。すなわち、本発明に用いる誘電体セラミック材料は、いわゆる高温焼成用のものであり、焼成に伴ない内部導体が溶融するとともに、セラミック材料が焼結体を形成するところに本発明の特徴がある。従って、本発明では、内部導体の融点以上の温度であって、かつセラミック材料の焼結終了温度以上の温度で焼成する。

【0015】本発明にいう「焼結終了温度」とは、理論的にセラミック材料が焼結体を形成する温度を指し、後述のように熱収縮曲線から求められるものである（後記図1参照）。

【0016】本発明における焼結終了温度は、上記のように、内部導体の融点以上の温度であり、好ましくは内部導体の融点+50℃以上、さらに好ましくは内部導体の融点+100℃以上、特に好ましくは内部導体の融点+150℃以上の温度である。また、後述の熱収縮曲線から求められる焼結開始温度（図1：点C）と焼結終了温度 T_s （図1：点F）間において点Cから80%のところに相当する温度 T_g （図1：点G）が、内部導体の融点以上の温度が好ましく、さらには内部導体の融点+20℃以上の温度が好ましく、特に内部導体の融点+50℃以上の温度であることが好ましい。また、あまりに蒸気圧が高くなるほどの高温となると内部導体が蒸発してしまうので、焼結終了温度の上限は、上記のように内部導体の沸点以下とする。通常、焼結終了温度は960～1900℃、好ましくは1100～1700℃程度である。なお、上記における内部導体の融点、沸点は、内部導体金属（合金も含む。）の融点、沸点であり、通常バルク状態で求められたものである。

【0017】また、実際の焼結温度は焼結終了温度以上の温度とする。ただし、この関係は、実際の焼成温度に到達するまでの昇温速度と同条件とした熱収縮曲線から

$p \leq T_s \leq T_b$ の関係にあることが好ましい。

【0018】このように、本発明の多層セラミック部品は、誘電体セラミック材料として内部導体の融点以上の温度で焼結するものを用い、誘電体セラミック材料の焼結終了温度以上の温度で焼成しているので、内部導体から焼成時に発生するガスを誘電体セラミック材料層外に排出することができる。従って、表面に凹凸がなく、表面状態が良好な内部導体を形成することができる。このため、共振器としてのQ値等の特性が高くなる。なお、このとき発生するガスは焼成時に発生するもので、例えばバインダや溶剤等のビヒクルに由来して発生する炭酸ガスや水分等のガスである。

【0019】また、従来、誘電体セラミック材料層と内部導体を積層して同時焼成する方法を採用する場合、内部導体の溶融を防止するため、内部導体の融点より高い温度で焼結するセラミック材料は用いることができないとされており、誘電率およびQ・f値に優れた材料であっても焼成温度が高いため用いることができないとされていた（特開平3-290358号等）。しかしながら、本発明では、内部導体を溶融状態とすることによって、内部導体の構造を緻密化し、導体の接触状態を改善し、線路の損失を低減させ、共振器としてのQ値を向上させる効果を得ている。このため、焼結温度が高く、かつ誘電率およびQ・f値に優れたセラミック材料を用いることができ、セラミック材料自体の高特性を生かすことができ、共振器としてのQ値を高くすることができる。

【0020】なお、前記焼結終了温度が内部導体の融点未満の温度となると内部導体の表面性が良化する効果が得られなくなり、一方内部導体の沸点をこえる温度となると内部導体が消失してしまう。また、焼成温度が内部導体の融点未満の温度となると、セラミック材料が未焼結のままであり、かつ内部導体溶融による効果が得られない。

【0021】前記の「焼結終了温度」は、図1に示すような熱収縮曲線から求められるものである。図1に示すように、温度の上昇に伴い、セラミック材料は、ある傾向をもって熱膨張するが、ある温度になるとその傾向からずればじめる。熱収縮曲線におけるその点をAとする。A点を過ぎてセラミック材料は収縮しはじめ、一定割合で収縮しはじめる。一定割合で収縮する領域の最低温側の点をBとする。また、一定割合で収縮する領域の最高温側の点をDとする。さらに、収縮が終了し、体積変化がほとんどないと考えられる領域のうち最低温側の点をEとする。

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体セラミック材料としては、焼結終了温度が前記した条件を満たすものであれば、本発明のようなものであってもよく、特に限定しない。しかし、例えば200MHz～10GHz程度の周波数を扱う高周波用共振器等の誘電体層として用いる場合、焼成して得られる誘電体セラミック材料に窒化物や炭化ケイ素系のセラミック等を用いた例は無い。また、窒化物や炭化ケイ素系のセラミックでは、それらの材料と内部導体として用いる銀や銅あるいはそれらを含む合金等の熔融金属との濡れ性が悪い。小型化、薄層化する傾向にある多層セラミック部品ではその内部導体層も厚さを薄く、さらに幅も狭くする必要性が高くなっている。このような多層セラミック部品の焼成に際し、濡れ性の悪いセラミック材料を用いた誘電体セラミック層では内部導体層の断線等の欠陥の発生率が高くなりやすい。そのため、誘電体セラミック材料としては、濡れ性がより高く、内部導体層の断線等の欠陥の発生率が低い、焼成により酸化物または酸化物の混合物となるものが好ましい。例えば後述する材料系を用いて焼成して得られた複合酸化物や、一部にルチル構造等を有する酸化物の混合物等である。本発明は、このような誘電体セラミック材料を焼成して得られた、酸化物や酸化物の混合物の誘電体セラミック層をもつ多層セラミック部品である。

【0024】本発明に用いる誘電体セラミック材料の具体例としては、 $MgO-SiO_2$ 系、 $CaO-MgO-TiO_2$ 系、 $BaO-TiO_2-SnO_2$ 系、 $BaO-MgO-CoO-Nb_2O_5$ 系、 $BaO-Nd_2O_3-TiO_2-Bi_2O_3-Al_2O_3-MnO$ 系などが挙げられる。 $MgO-SiO_2$ 系としては、 $2MgO \cdot SiO_2$ 30～95モル%、 $CaTiO_3$ 50モル%以下、 $SrTiO_3$ 60モル%以下で、これら各酸化物の合計100モル%に対し、 MgO を0.1～10wt%、 La_2O_3 を0.1～10wt%添加したもの（特開昭47-21698号参照）； $CaO-MgO-TiO_2$ 系としては、 $MgTiO_3$ 70～100モル%、 TiO_2 0～30モル%で、これら各酸化物の合計100モル%に対し、 $CaTiO_3$ を1～9wt%添加したもの（特開昭52-118599号）； $BaO-TiO_2-SnO_2$ 系としては、 $BaO \cdot x \{ (1-y)TiO_2 \cdot ySnO_2 \}$ [$x=4 \sim 4.5$, $y=0 \sim 0.10$]の組成を有するもの（特公平4-32483号参照）； $BaO-MgO-CoO-Nb_2O_5$ 系としては、 BaO 56.0～63.0wt%、 CoO 0.1～11.7wt%、 MgO 0.1～6.5wt%、 Nb_2O_5 31.0～34.0wt%のものを（特開昭52-70070号参照）；

%、 MnO を0.1～1.0wt%添加したもの（本出願人による特願平3-327352号）である。このほか、 $BaO-MgO-Ta_2O_5$ 系、 $ZrO_2-SnO_2-TiO_2$ 系、 $PbO-CaO-ZrO_2$ 系、 $SrO-ZrO_2-TiO_2$ 系、 $BaO-Sm_2O_3-TiO_2$ 系、 $PbO-BaO-Nd_2O_3-TiO_2$ 系、および $Li_2O-Na_2O-Sm_2O_3-TiO_2$ 系等も用いることができる。

【0025】 $BaO-MgO-Ta_2O_5$ 系としては、例えば $Ba_x(Mg_{1-x}Ta_x)_2O_7$ 、ただし0.28 ≤ x ≤ 0.39、0.98 ≤ y ≤ 1.00の組成式で示されるものである。 $ZrO_2-SnO_2-TiO_2$ 系としては、例えば $(Zr_{1-x}Sn_x)_2TiO_7$ 、ただし0.1 ≤ x ≤ 0.3の組成式で示されるものである。 $PbO-CaO-ZrO_2$ 系としては、例えば $(Pb_{1-x}Ca_x)_2ZrO_7$ 、ただし0.35 ≤ x ≤ 0.5の組成式で示されるものである。 $SrO-ZrO_2-TiO_2$ 系としては、例えば $Sr_x(Zr_{1-x}Ti_x)_2O_7$ 、ただし0 ≤ x ≤ 0.1、0.98 ≤ y ≤ 1.01の組成式で示されるものである。 $BaO-Sm_2O_3-TiO_2$ 系としては、 $xBaO \cdot ySm_2O_3 \cdot zTiO_2$ として、0.1 ≤ x ≤ 0.2、0.1 ≤ y ≤ 0.2、0.6 ≤ z ≤ 0.75のものである。 $PbO-BaO-Nd_2O_3-TiO_2$ 系としては、 $xBaO \cdot yNd_2O_3 \cdot zTiO_2$ として、0.02 ≤ x ≤ 0.25、0.05 ≤ y ≤ 0.41、0.50 ≤ z ≤ 0.82で、これら各成分の合計に対し、さらに PbO を17wt%以下含有するものである。 $Li_2O-Na_2O-Sm_2O_3-TiO_2$ 系としては、例えば $(Li_xNa_ySm_z)_2TiO_7$ 、ただしx+y+z=1として、0.25 ≤ x ≤ 0.35、0.15 ≤ y ≤ 0.25、0.4 ≤ z ≤ 0.6の組成式で示されるものである。

【0026】また、上記の基本組成に加えて、さらに、必要に応じ、 MnO 、 CuO 、 ZnO 、 SnO_2 、 PbO 、 NiO 、 WO_3 、 SiO_2 、 B_2O_3 、および Nb_2O_5 等が添加されていてもよい。

【0027】また、上記の誘電体セラミック材料は、20℃における比誘電率(ε)が6.5～120、特に20～120、誘電損失(Q・f値)が3500～225000、共振周波数温度係数(τf)が-4.5～+8.5ppm/℃のマイクロ波誘電特性を有する。なお、τfは-40℃の共振周波数と80℃の共振周波数を結んだ直線の傾きとして求めたものである。

【0028】本発明において、内部導体ペーストのパターン形成のための材料組成は、本発明の誘電体セラミック材料の組成と異なる。

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86. 5wt%. 好ましくは30~84wt%, B_2O_3 を8. 5~21wt%, 好ましくは9~19wt%, ZnO を5~50wt%. 好ましくは7~43wt%含有するガラスを用いることが好ましい。このようなガラスにおいて、さらに、 Al_2O_3 および/または SiO_2 を含有してもよく、これらのものを含有するときの含有量は、 Al_2O_3 が20wt%以下、好ましくは0. 1~5wt%, SiO_2 が9wt%以下、好ましくは2~7wt%とするのがよい。

【0029】このような誘電体のセラミック材料は、焼結前にビヒクルを加えてスラリーとされる。ビヒクルとしては、エチルセルロース、ポリビニルブチラール、メタクリル樹脂、ブチルメタアクリレート等のバインダ、テルピネオール、ブチルカルビトール、ブチルカルビトールアセテート、アセテート、トルエン、アルコール、キシレン等の溶剤、その他各種分散剤、活性剤、可塑剤等が挙げられ、これらのうち任意のものが目的に応じて適宜選択される。ビヒクルの添加量は、酸化物質材とガラスの合計量100重量部に対し、65~85wt%程度とすることが好ましい。

【0030】内部導体としては特に制限はないが、内部導体層の直流での導電率が $1 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ 以上の導体材料を用いることが好ましい。また導電率の上限には特に制限はないが、通常 $6. 2 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ 程度である。

【0031】具体的には、銀($6. 17 \times 10^3 \Omega^{-1} \text{cm}^{-1}$)、銅($5. 81 \times 10^3 \Omega^{-1} \text{cm}^{-1}$)を用いることが好ましい。より好ましい態様では、融点が960℃付近の銀または融点1060℃付近の銅を用いる。この際、銀あるいは銅の含有量が90wt%以上のもの、特に純度99wt%以上、さらには99. 9wt%以上の純銀または純銅を用いることが好ましい。このように、特に純銀ないし純銅を用いることにより導電率の逆数である比抵抗と損失とをきわめて小さくすることができ、共振器のQ値を向上させることができる。

【0032】従って、銀の場合は、その融点である960℃以上の温度であって、かつセラミック材料の焼結終了温度以上の温度で焼成することが好ましく、通常1150~1750℃、さらには1200~1700℃の温度とすることが好ましい。また、銅の場合は、その融点である1060℃以上の温度であって、かつセラミック材料の焼結終了温度以上の温度で焼成することが好ましく、銀の場合と同様に通常1150~1750℃、さらには1200~1700℃の温度とすることが好まし

場合には通常、空気中にて上記の温度で1分~1時間程度、より好ましくは、5~20分程度行なうことが好ましい。また、銅の場合には、通常、酸素分圧を 10^{-4}atm 以下に制御して行なう。なお、焼成は複数回行なってもよく、そのとき少なくとも1回は上記条件を満足する融点以上の焼成とする。

【0034】内部導体パターンの形成方法としては、所定形状の銀箔等を誘電体グリーンシートにはさむ、あるいは導体ペーストの印刷または転写を行なう等の方法が挙げられるが、特に印刷法が好ましい。

【0035】導体ペーストにてパターンを形成する場合、用いる銀箔、銅粉等の導体粉の平均粒径(異方性のある時には長軸径)は、0. 5~20 μm 程度、より好ましくは1~5 μm とするのが好ましい。粒径が小さすぎると、分散性が悪くなり、導体ペースト中の導体粉の含有量を多くすることができず、また含有量を多くすると粘度が高くなってしまい、緻密なパターンを形成できなくなってくる。一方、粒径が大きすぎると、スクリーン印刷、転写法等によるパターンの形成が困難となってくる。また、銀箔の形状等には特に制約はないが、一般に球状とし、その一部または全部を鱗片状のものとしてもよい。

【0036】内部導体ペースト中の導体粉の含有量は、60~95wt%、特に70~90wt%とするのが好ましい。含有量が少ないと、比抵抗が減少し、Q値が低下し、焼成後のパターンの一部が断線したり、比抵抗やQ値がばらついたりしてくる。また大きすぎると、ペーストの粘度が増大し、パターン形成が困難となってくる。

【0037】また、内部導体のペーストにはガラスフリットを添加してもよく、特に導体粉融点付近に軟化点をもつガラスフリットを添加することが好ましい。このようなガラスフリットを添加することにより、溶融後の網目構造の発生が減少し、Q値のバラツキを抑えることができる。

【0038】特に、ガラスフリットの添加は平均粒径の小さい微粉末の導体材料を用いたときに内部導体材料の拡散を防止する上で、有効であり、比較的大径の導体材料では拡散はそれほど問題とはならず、この場合はガラスフリットの添加はしない方が好ましい。ガラスフリットを添加しない方が伝送線路の損失をさらに低減することができる。

【0039】内部導体ペースト中のガラスフリットを添加する場合、その含有量は、10wt%以下、特に1~10wt%、さらには3~8wt%が好ましい。また、ガラスフリットは、導体粉に比べて、融点が高いので、焼成の

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下2ヶ所ある。このうち少なくとも一方の内部導体層の最外層側の表面から最外層表面までの距離が前記以下の場合、剥離による事故が発生しやすい。なお、前記誘電体セラミック層の厚さは、通常40 μ m以上で用いられる。

【0052】このような場合、焼成時の酸素分圧を、前記 1×10^{-1} atm以下、より好ましくは 5×10^{-1} atm以下、特に 1×10^{-1} atm以下とすることが好ましい。すなわち、焼成時に積層方向の最外層にある前記誘電体セラミック材料層の厚さが薄いほど、銀導体の冷却固化時に放出される酸素ガスによる、導体と誘電体セラミック層の間の内圧上昇の影響を受けて割裂が発生しやすいため、誘電体セラミック材料層の厚さが薄いほど焼成時の酸素分圧を低くすることが好ましい。

【0053】ただし、焼成時の酸素分圧を低くする場合、前記した誘電体セラミック材料のうち、CaO-MgO-TiO₂系、BaO-TiO₂-SnO₂系、BaO-Nd₂O₃-TiO₂-Bi₂O₃-Al₂O₃-MnO系、ZrO₂-SnO₂-TiO₂系、SrO-ZrO₂-TiO₂系、BaO-Sm₂O₃-TiO₂系、PbO-BaO-Nd₂O₃-TiO₂系、Li₂O-Na₂O-Sm₂O₃-TiO₂系、等は、焼成時の酸素分圧が、 1×10^{-1} atm以下では還元されやすくなる。誘電体セラミック材料が還元されると例えば共振器等の部品を構成した場合、そのQ値が著しく低下することになる。このため、これらの組成の誘電体セラミック材料を用い、さらに焼成時に積層方向の最外層表面と内部導体層の最外層側の表面との距離が前記500 μ m以下の構成をもつ多層セラミック部品は、 1×10^{-1} atmを超え、 1×10^{-1} atm以下、より好ましくは 5×10^{-1} atm～ 1×10^{-1} atm、特に 1×10^{-1} ～ 1×10^{-1} atmの酸素分圧下で焼成することが好ましい。

【0054】また、特に銅を導体材料とする場合、前記のように、通常は酸素分圧を 1×10^{-1} atm以下に制御して行なう。酸素分圧が高すぎると銅の酸化により内部電極が消失してしまうことがある。

【0055】しかし、前記のように、誘電体セラミック材料によっては酸素分圧を低下させると還元される材料がある。このため、内部導体に銅を用いる場合は、酸素分圧を低下させても還元されにくい材料を用いることが好ましい。このような材料としては、MgO-SiO₂系、BaO-MgO-CoO-Nb₂O₅系およびPbO-CaO-ZrO₂系等が挙げられる。

【0056】本発明の多層セラミック部品は共振器としてのQ値が高いものであり、誘電体の厚さ2 μ mの条件で

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であり、誘電体セラミック材料の素体11に、内部導体21、22および23が図示のように間隔されたものである。

【0059】また、図3に示す構成のものであってもよく、フィルター2は誘電体セラミック材料の素体11に、内部導体25および26が図示のように並列に間隔されたものである。

【0060】なお、図2、図3のいずれのフィルターにおいても、外表面は金属や絶縁材で被覆されている。

【0061】またさらに、図4に示す構成のものであってもよい。図4では、積層方向の最外層に誘電体セラミック層を有し、内部導体層27および29が前記積層方向の最外層表面から500 μ m以下の距離に配置されている。このように、最外層の誘電体セラミック層の厚さ1 μ mの少なくとも一方が、焼成後500 μ m以下で、さらに内部導体層27や29に銀を用いる場合、前記のように、最外層の誘電体セラミック層が内部導体層27や29と割裂しやすくなる。なお、図4に示すフィルターでは、内部導体層27、29がシールド層として機能するので通常外表面に、外部電極は設けない。

【0062】このような積層型フィルターは、誘電体セラミック材料の仮焼粉を用いてドクターブレード法などによりグリーンシートを成型し、それに所定のパターンで内部導体材料のペーストをスクリーン印刷法などにより印刷し、印刷したシートを積層して熱プレスにより熱圧着し、脱バインダー後、内部導体の融点以上の温度であって、かつセラミック材料の焼結終了温度以上の温度で焼成して得ることができる。その後、必要に応じて外部電極用ペーストを印刷し、外部電極を焼き付けするなどすればよい。このほか、印刷積層法によってもよい。

【0063】このようにして得られる積層型フィルターは誘電体の全体の厚さが0.5～4mm程度である。また内部導体の厚さは20～100 μ m程度、幅は0.5～2mm程度である。この際、厚さ50 μ m以下、さらに40 μ m以下のときに本発明の効果は倍加する。また、誘電体セラミック層の厚さは、40～150 μ m程度である。なお、本発明の多層セラミック部品は、通常200MHz以上、特に800MHz～10GHz程度の周波数帯域で用いられる。

【0064】

【実施例】以下、本発明を実施例によって具体的に説明する。

【0065】実施例1

表1に示す各々の組成で、仮焼、粉碎、スラリー調製、ドクターブレード法により500 μ mの厚さのグリーンシートを成型し、それに所定のパターンで内部導体材料のペーストをスクリーン印刷法などにより印刷し、印刷したシートを積層して熱プレスにより熱圧着し、脱バインダー後、内部導体の融点以上の温度であって、かつセラミック材料の焼結終了温度以上の温度で焼成して得ることができる。その後、必要に応じて外部電極用ペーストを印刷し、外部電極を焼き付けするなどすればよい。このほか、印刷積層法によってもよい。

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ルA～I)を各々作製した(表1)。このときの積層数は20層とした。

【0066】1/4λ共振器においては、内部導体の厚さが60μm、幅が2mmであった。

【0067】また、誘電体の厚さは表1に示すように3.0mmとした。

【0068】全体の寸法は1/4λ(誘電体中における*

銀粉(平均粒径3μm:純度99.9%以上) 90wt%

アクリル樹脂(バインダー)

タービネオール(溶剤)

2.5wt%

7.5wt%

【0071】さらに、上記のように作製した1/4λ共振器のフィルタ特性はYHP8510ネットワークアナライザで評価し、共振器としてのQ値を求めた。結果を表1に示す。

【0072】なお、上記における誘電体セラミック材料のグリーンシートの作製は、特開昭47-21698号、特開昭52-118599号、特開昭61-72676号、特公平4-32483号、本出願人による特願平3-327352号の方法などに準じて行なった。その際の仮焼条件は表2に示すとおりとした。

【0073】また、上記において、グリーンシートを作製するかわりに、円柱状に成型し、表2に示す焼成条件

*波長λの1/4)×5mm×3.0mmとした。

【0069】なお、上記において用いたAg導体ペーストは、以下に示す組成のものを三本ロールにより混合分散して得たものである。なお、表1にはAgの融点および導電率を示す。

【0070】

として焼成し、サンプルを得た(サンプルNo.1～8)。これらのサンプルを10mmφ×5mmに加工したのち誘電体共振法にて誘電率(ε)、Q・f値を求めた。また-40℃の共振周波数と80℃の共振周波数を結んだ直線の傾きを求め、共振周波数温度係数(τf)を算出した。結果を表2に示した。

【0074】さらに、各材料につき、200℃/時間の昇温速度における熱収縮曲線から焼結終了温度(℃)および焼結開始温度(℃)を求め、表3に示した。

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【表1】

表 1

サンプル	誘電体セラミックス材料 組成	材料	導体材料 融点	導電率 ($\Omega^{-1}\text{cm}^{-1}$)	焼成条件 温度 時間 雰囲気	共振特性 Q値	誘電体 厚さ
A	2MgO·SiO ₂ -CaTiO ₃ -SrTiO ₃ (90wt%) (2wt%) (8wt%) -MgO - La ₂ O ₃ (1.5wt%) (1.5wt%)	Ag	960°C	6.17×10^5	1230°C 10分 大気中	338	3mm
B	MgTiO ₃ -TiO ₂ -CaTiO ₃ (90wt%) (10wt%) (6.2wt%)	Ag	960°C	6.17×10^5	1380°C 10分 大気中	418	3mm
C	BaO - CoO - MgO - Nb ₂ O ₅ (58.8wt%) (4.8wt%) (2.5wt%) (33.8wt%)	Ag	960°C	6.17×10^5	1470°C 10分 大気中	390	3mm
D	BaO·x [(1-y)TiO ₂ ·ySnO ₂] (x=4.4, y=0.09)	Ag	960°C	6.17×10^5	1360°C 10分 大気中	316	3mm
E	BaO - TiO ₂ - Nd ₂ O ₃ (14.7wt%) (70.0wt%) (15.3wt%) - Bi ₂ O ₃ - Al ₂ O ₃ - MnO (7.5wt%) (1.0wt%) (0.1wt%)	Ag	960°C	6.17×10^5	1320°C 10分 大気中	322	3mm
F	BaO·x [(1-y)TiO ₂ ·ySnO ₂] (x=4.4, y=0.09)	Ag	960°C	6.17×10^5	1360°C 10分 大気中 1 × 10 ⁻³ 気圧 (0.2分圧)	368	3mm
G	Ba(Mg _{1/3} Ta _{2/3})O ₃	Ag	960°C	6.17×10^5	1670°C 10分 大気中	420	3mm
H	(Zr _{0.95} Sn _{0.05})TiO ₄	Ag	960°C	6.17×10^5	1600°C 10分 大気中	388	3mm
I	(Pb _{0.95} Ca _{0.05})ZrO ₃	Ag	960°C	6.17×10^5	1450°C 10分 大気中	300	3mm

[0076]

[表2]

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表 2

サンプル No.	誘電体セラミック材料 組成	仮焼条件 温度 (℃)	焼成条件 温度 (℃)	時間	ϵ	$Q \cdot f$ (GHz)	τf (ppm/℃)
1	2NbO ₃ ·SiO ₂ -CaTiO ₃ -SrTiO ₃ (90wt%) (2wt%) (8wt%) -MgO - La ₂ O ₃ (1.5wt%) (1.5wt%)	1000	1230	2時間 10分	7	13000	0
2	MgTiO ₃ -TiO ₂ -CaTiO ₃ (90wt%) (10wt%) (6.2wt%)	1100	1380	3時間 10分	20	40500	0
3	BaO - CoO - MgO - Nb ₂ O ₅ (58.8wt%) (4.8wt%) (2.6wt%) (33.8wt%)	1200	1470	2時間 10分	33	70000	-4.0
4	BaO·x [(1-y)TiO ₂ ·ySnO ₂] (x=4.4, y=0.09)	1100	1360	2時間 10分	37	35000	+4.0
5	BaO - TiO ₂ - Nd ₂ O ₃ (14.7wt%) (70.0wt%) (15.3wt%) - Bi ₂ O ₃ - Al ₂ O ₃ - MnO (7.5wt%) (1.0wt%) (0.1wt%)	1200	1320	2時間 10分	93	4000	+8.0
6	Ba(Mg _{1/3} Ta _{2/3})O ₃	1300	1670	2時間 10分	21	220000	+4.0
7	(Zr _{0.6} Sn _{0.4})TiO ₄	1200	1600	2時間 10分	38	55000	0
8	(Pb _{0.95} Ca _{0.05})ZrO ₃	1000	1450	2時間 10分	110	3300	+13

[0077]

[表3]

表 2

サンプル No.	誘電体セラミック材料 組成	仮焼条件 温度 (°C) 時間	焼成条件 温度 (°C) 時間	ϵ	$Q \cdot f$ (GHz)	τf (ppm/°C)
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1	2MgO-SiO ₂ -CaTiO ₃ -SrTiO ₃ (90wt%) (2wt%) (8wt%) -MgO - La ₂ O ₃ (1.5wt%) (1.5wt%)	1000 2時間	1230 10分	7	13000	0
2	MgTiO ₃ -TiO ₂ -CaTiO ₃ (90wt%) (10wt%) (5.2wt%)	1100 3時間	1380 10分	20	40500	0
3	BaO - CoO - MgO - Nb ₂ O ₅ (58.8wt%) (4.8wt%) (2.6wt%) (33.8wt%)	1200 2時間	1470 10分	33	70000	-4.0
4	BaO · x [(1-y)TiO ₂ · ySnO ₂] (x=4.4, y=0.09)	1100 2時間	1360 10分	37	35000	+4.0
5	BaO - TiO ₂ - Nd ₂ O ₃ (14.7wt%) (70.0wt%) (15.3wt%) - Bi ₂ O ₃ - Al ₂ O ₃ - hmf (7.5wt%) (1.0wt%) (0.1wt%)	1200 2時間	1320 10分	93	4000	+8.0
6	Ba (Mg _{1/3} Ta _{2/3})O ₃	1300 2時間	1670 10分	21	220000	+4.0
7	(Zr _{0.8} Sn _{0.2})TiO ₄	1200 2時間	1600 10分	38	55000	0
8	(Pb _{0.85} Ca _{0.15})ZrO ₃	1000 2時間	1450 10分	110	3300	+13
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[0077]

[表 3]

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表 3

サンプル No.	誘電体セラミック材料 組 成	焼結終了温度 (昇温速度: 200℃/hr)	焼結開始温度
1	2MgO·SiO ₂ -CaTiO ₃ -SrTiO ₃ (90wt%)(2wt%)(8wt%) -MgO - La ₂ O ₃ (1.5wt%)(1.5wt%)	1226℃	1141℃
2	MgTiO ₃ -TiO ₂ -CaTiO ₃ (90wt%)(10wt%)(6.2wt%)	1357℃	1179℃
3	BaO - CoO - MgO - Nb ₂ O ₅ (58.8wt%)(4.8wt%)(2.6wt%)(33.8wt%)	1468℃	1306℃
4	BaO·x [(1-y)TiO ₂ ·ySnO ₂] (x=4.4, y=0.09)	1307℃	1172℃
5	BaO - TiO ₂ - Nd ₂ O ₃ (14.7wt%)(70.0wt%)(15.3wt%) - Bi ₂ O ₃ - Al ₂ O ₃ - MnO (7.5wt%)(1.0wt%)(0.1wt%)	1282℃	1154℃
6	Ba(Mg _{1/3} Ta _{2/3})O ₃	1652℃	1523℃
7	(Zr _{0.8} Sn _{0.2})TiO ₄	1580℃	1445℃
8	(Pb _{0.65} Ca _{0.35})ZrO ₃	1427℃	1281℃

【0078】表1の結果から明らかなように、本発明の1/4λ共振器は高いQ値を示している。従来、誘電体セラミック材料と導体材料とを同時焼成して積層フィルタを作製する場合、内部導体材料を溶融しない温度で焼成する必要があり、上記で用いているような高温焼成用のものは用いることができないとされていた(特開平3-290358号等)が、これを覆す事実が明らかになった。

【0079】実際、例えば、特開平3-295856号実施例6に開示された低温焼成用のセラミック材料(200℃/時間の昇温速度における焼結終了温度は925℃以下と推定される。)を用いるほかは同様にして、上記と同様に1/4λ共振器を作製し、Q値を求めたところ、本発明のものより明らかに低いQ値を示すことがわかった。

【0080】実施例2

表1に示すサンプルE、HおよびIの組成を用い、図4の構成要素(1)〜(4)の焼成条件を、表3の通りとした。

【0081】さらに、サンプルEの組成を用い、焼成雰囲気は酸素分圧を表4に示す条件とし、図4に示す積層方向表面の誘電体セラミック材料層の厚さ*t*、*t'*を、焼成後400μmとなるようにして、サンプルNo. 25および26を作製した。

【0082】得られたそれぞれの焼成物の積層方向表面の誘電体セラミック材料層の剥離状況を評価し、結果を表4に示した。

【0083】次いで、剥離の認められなかったサンプルについて、1/4λ共振器を作製した。このときの積層数は、内部導体27と29との間で20層とした。1/4λ共振器においては、内部導体28の厚さが60μm、幅が2mmであった。また、共振器部分の誘電体の厚さは表1に示すように3.0mmとした。共振器部分の全体の寸法は1/4λ(誘電体中における波長λの1/4)×5mm×3.0mmとした。

【0084】得られたそれぞれの共振器のフィルタ特性を、表4の通りとした。

【表4】

表 4

サンプル No.	誘電体セラミック材料組成	内蔵導体 材料	焼成雰囲気 (酸素分圧) (atm)	内蔵導体と誘電体 セラミック材料層 との剥離の有無	共振器特性 Q値	セラミック 材料層厚さ t (μm)
2 1 (比較)	BaO -TiO ₂ -Nd ₂ O ₃ -Bi ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (7.5wt%) (1.0wt%) (0.1wt%)	Ag	大気中	剥離発生	322	200
2 2	BaO -TiO ₂ -Nd ₂ O ₃ -Bi ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (7.5wt%) (1.0wt%) (0.1wt%)	Ag	1×10 ⁻³	剥離なし	320	200
2 3	BaO -TiO ₂ -Nd ₂ O ₃ -Bi ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (7.5wt%) (1.0wt%) (0.1wt%)	Ag	1×10 ⁻³	剥離なし	306	200
2 4 (比較)	BaO -TiO ₂ -Nd ₂ O ₃ -Bi ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (7.5wt%) (1.0wt%) (0.1wt%)	Ag	1×10 ⁻⁴	剥離なし	161	200
2 5 (比較)	BaO -TiO ₂ -Nd ₂ O ₃ -Bi ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (7.5wt%) (1.0wt%) (0.1wt%)	Ag	大気中	剥離発生	322	400
2 6	BaO -TiO ₂ -Nd ₂ O ₃ -Bi ₂ O ₃ -Al ₂ O ₃ -MnO (14.7wt%) (70wt%) (15.3wt%) (7.5wt%) (1.0wt%) (0.1wt%)	Ag	1×10 ⁻³	剥離なし	318	400
3 1 (比較)	(Zr _{0.8} Sn _{0.2})TiO ₄	Ag	大気中	剥離発生	338	200
3 2	(Zr _{0.8} Sn _{0.2})TiO ₄	Ag	1×10 ⁻³	剥離なし	384	200
3 3	(Zr _{0.8} Sn _{0.2})TiO ₄	Ag	1×10 ⁻³	剥離なし	352	200
3 4 (比較)	(Zr _{0.8} Sn _{0.2})TiO ₄	Ag	1×10 ⁻⁴	剥離なし	140	200
4 1 (比較)	(Pb _{0.85} Ca _{0.15})ZrO ₃	Ag	大気中	剥離発生	300	200
4 2	(Pb _{0.85} Ca _{0.15})ZrO ₃	Ag	1×10 ⁻³	剥離なし	310	200
4 3	(Pb _{0.85} Ca _{0.15})ZrO ₃	Ag	1×10 ⁻³	剥離なし	298	200
4 4	(Pb _{0.85} Ca _{0.15})ZrO ₃	Ag	1×10 ⁻⁴	剥離なし	292	200
4 5	(Pb _{0.85} Ca _{0.15})ZrO ₃	Ag	1×10 ⁻³	剥離なし	288	200
4 6	(Pb _{0.85} Ca _{0.15})ZrO ₃	Ag	1×10 ⁻⁴	剥離なし	281	200

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ック材料の焼結終了温度 T_{2e} は、いずれも、Agの融点+150℃以上の温度であり、また熱収縮曲線から求めた焼結開始温度（図1：点C）と焼結終了温度 T_{2e} （図1：点F）との距離において点Cから80%のところに相当する温度 T_{2e}' （図1：点G）はAgの融点+50℃以上の温度であることが確認された。

【0088】実施例3

誘電体セラミック材料として、表1に示すサンプルA、DおよびEを用い、それぞれの組成で実施例1と同様にグリーンシートを成型し、それに実施例1と同じAg導体ペーストを用いてスクリーン印刷法により直線パターンを印刷した。印刷したシート上に、さらに、それぞれ同じ誘電体セラミック材料のグリーンシートを積層熱圧着して脱バインダー後、焼成雰囲気中の酸素分圧を 1×10^{-1} とし、他は表1に示すそれぞれの誘電体セラミック材料の焼成条件により焼成し、焼成体を得た。

【0089】焼成体のサイズは、縦5.6mm、横6.5mm、厚さ400 μ mとした。また、Ag導体は、焼成体縦方向に1焼成体あたり24本をほぼ等間隔で配置し、導体の直線パターンは、焼成後のサイズで長さ約4.6mm、幅約1mm、厚さ約40 μ mとなるように印刷した。なお、導体の印刷場所は、積層後外部に露出しない位置とした。

【0090】得られたそれぞれの焼成体（誘電体セラミック材料1組成あたり10個作製した）を透明ガラス板上に置き、ガラス板下部から可視光源を照射して透過光を目視による観察と分析法による透過X線像の観察とを行い、Ag導体の断線部分の有無を調べた。その結果、断線部分はそれぞれの誘電体セラミック材料の試料について1焼成体あたり5～10ヶ所であった。

*39 【0096】

銅粉（平均粒径5 μ m：純度99.9%以上） 90wt%

アクリル樹脂（バインダー） 2.5wt%

ターピネオール（溶剤） 7.5wt%

【0097】得られたそれぞれの共振器は、良好な共振器特性（Q値）を示した。

【0098】

【発明の効果】本発明によれば、内部導体を緻密化し、しかも表面性を良好にすることができ、かつ誘電率および誘電損失（ $Q \cdot f$ ）等に優れた誘電体セラミック材料を用いることができ、この結果Q値等の特性の向上を図ることができる。さらに、焼成時に内部導体層と誘電体セラミック層との剥離による不良品の発生や、内部導体層の断線等の発生を減少させることができる。

【図面の簡単な説明】

【図1】焼結終了温度の示した説明書中の熱収縮

*【0091】比較例1

誘電体セラミック材料として、平均粒径約1 μ mの窒化アルミニウム粉末を用い、さらに焼結助剤としてCaO換算で0.5wt%となる量の炭酸カルシウムを加え、バインダー等とともにスラリーとしてグリーンシートを作成した。Ag導体ペーストを用い、実施例3と同様のパターンを同様に印刷し、さらに同じグリーンシートを積層熱圧着して脱バインダー後、窒素ガス雰囲気中で温度1600℃、10分焼成して焼成体を得た。なお、焼成体や導体のサイズ、導体のパターンや印刷位置等は実施例3と同じとした。

【0092】得られた10個の焼成体について、実施例3と同様にAg導体の断線部分の有無を調べた。その結果、断線部分は1焼成体あたり40～50ヶ所であり、さらに断線まで至らないが、導体の幅が狭窄した部分が多数認められた。

【0093】実施例3および比較例1より明らかなように、酸化物または酸化物の混合物を誘電体セラミック材料として用いた場合、熔融金属との濡れ性の悪い窒化アルミニウムを用いた場合と比較して、導体の断線事故発生率が大きく低下する。

【0094】実施例4

内部導体材料として銅を用い、誘電体セラミック材料として表1のサンプルA、CおよびIの組成を用い、焼成雰囲気として酸素分圧を 1×10^{-1} としたほかは実施例1と同様に共振器を作成した。

【0095】なお、用いたCu導体ペーストは、以下に示す組成のものを三本ロールにより混合分散して得たものである。

銅粉（平均粒径5 μ m：純度99.9%以上） 90wt%
アクリル樹脂（バインダー） 2.5wt%
ターピネオール（溶剤） 7.5wt%

曲線を示すグラフである。

【図2】本発明における積層型フィルタを模式的に示す概略構成図である。

【図3】本発明における積層型フィルタを模式的に示す概略構成図である。

【図4】本発明における積層型フィルタを模式的に示す概略構成図である。

【符号の説明】

1、2、3 積層型フィルタ

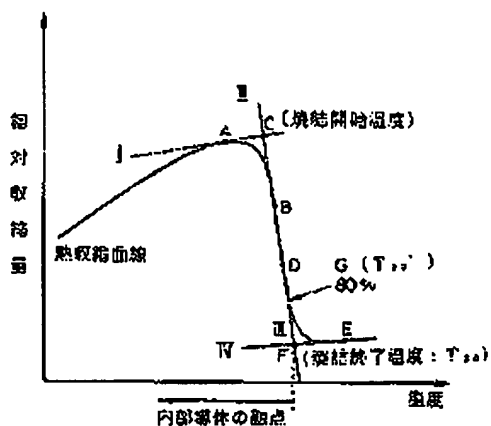
11 誘電体セラミック材料の素体

21～23、25～29 内部導体

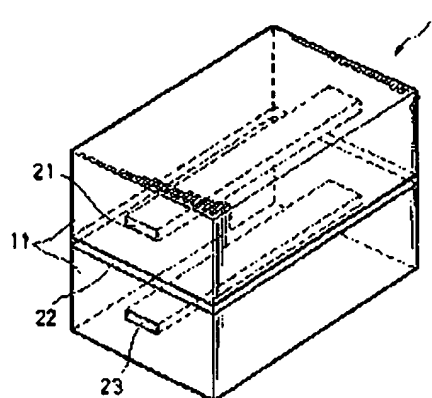
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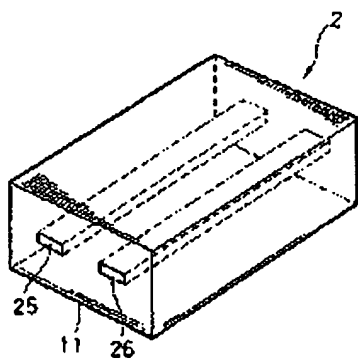
【図1】



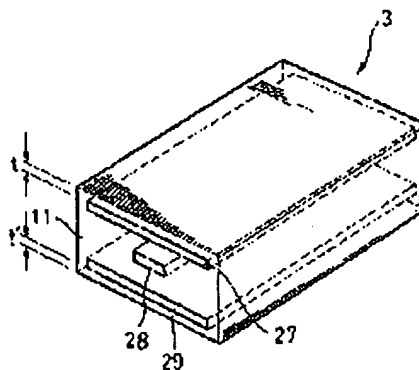
【図2】



【図3】



【図4】



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H 6921-4E

T 6921-4E

(72) 発明者 川村 敬三

東京都中央区日本橋一丁目13番1号 ティー

ディーケー株式会社内

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